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Measurements of the Chemical Composition of Western Washington Rainwater, 1982-1983

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16. Abstract (Limit: 200 words)

Precipitation was sampled for one year, 2/82 until 2/83 at four sites west of the Cascade Mountains in the state of Washington. Wet samples of one week duration were analyzed for sulfate, nitrate, ammonium, chloride, calcium, sodium, potassium, magnesium, arsenic, lead, zinc, cadmium, copper and phosphate. Measurements were also made of pH, conductivity and rain volume. The precipitation was found to be acidified (volume weighted average pH 4.4-4.5 at two sites in Seattle and 45-4.6 at two rural sites 39 km east and 120 km north of Seattle; the minimum measured pH was 3.5) with the acidification more closely associated with sulfate than nitrate. The three southern sites, two in Seattle, and one 30 km east of Seattle at Tolt River, had similar annual sulfate deposition of 1.3 to 1.7 gm per square meter. The site 120 km north of Seattle (5 km north of Bellingham) had precipitation that was less acid and annual sulfate deposition of 0.9 gm per square meter. The volume weighted conductivity of precipitation concentrations of arsenic, potassium, copper, zinc, and cadmium each averaged less than 6 micro-grams per liter but results showed poor reproducibility.

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Measurements of The Chemical Composition of Western Washington Rainwater, 1982-1983

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July 29, 1983

Sponsored by U.S. Environmental Protection Agency, Region 10, Seattle. U.S. Geological Survey, Tacoma, loaned precipitation sampling equipment to this program. Seattle Water Department provided three sampling sites.

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Contents

I	Executive Summary	1
II	Summary of Results of Precipitation Sampling and Chemical Analysis in Western Washington	6
III	Chemical Composition of Western Washington Rainwater	9
IV	Chemical Relationships in Western Washington Precipitation	12
V	Seasonal Variability	39
VI	Relation of Emissions to Rainwater Composition	44
VII	Measurements by Other Investigators	48
VIII	Conclusions and Recommendations	51
IX	References	54
X	Appendices	57

I Executive Summary

Acid Rain is now an important environmental, political and economic problem for the United States. Environmental impacts have been reported including failure of fish populations to reproduce, reduced growth rate or even die-back of forest tree species and leaching of nutrient or toxic ionic species from soils into water systems. In June of 1983, reports on acid rain were released by the National Research Council of the National Academy of Sciences (NAS), by a review panel created by George Kenworth, White House science advisor and by a federal Interagency Task Force on Acid Rain. The three reports agreed that in impacted areas such as the north-east United States and eastern Canada, acid rain is almost entirely caused by man with sulfur dioxide emissions making a larger contribution than oxides of nitrogen. The NAS and White House sponsored reports also concluded that acid deposition over large areas is in direct proportion to the up wind regional emission of acid forming species and that the effects of acid rain are damaging to the environment and must be reduced. The chairman of the White House panel, W. A. Nierenberg, speaking about impacts of acid deposition on soil micro-organisms that recycle nitrogen and carbon in the food chain, said that some of the effects of acid rain are severe, perhaps irreversible (Science; 15 July, 1983; pgs 241, 242 and 254).

Acid rain is also a political and economic problem because emissions in one area affect a large downwind region that often extends across political boundaries and because control of emissions will have high costs.

Because of its potential importance as an environmental, political and economic problem to this area, Region X of the U. S. Environmental Protection Agency funded the University of Washington to conduct the first year of a continuing program to determine the acid character of precipitation in Washington State west of the Cascade mountains. Four sites, two in Seattle (Maple Leaf and West Seattle Reservoirs of the Seattle water supply system), one 50 km east of Seattle (Tolt Reservoir of the Seattle water supply system) and one near the Canadian border (2 km north of Bellingham), were chosen to measure wet deposition on regions of sensitive lakes, on farming and forest areas and to measure deposition in an area that could be affected by sources in both the United States and Canada. The methods used in sampling and analysis of samples were chosen to be compatable with the nation-wide National Atmospheric Deposition Program (NADP) so that our rain quality could be compared to that in other areas. The precipitation was sampled 25 January, 1982 through 15 February, 1983. Sampling continues at three sites (the West Seattle site has been dropped) under support of EPA. The parameters measured include: rain volume, pH and conductivity. The samples were analyzed by the EPA laboratory at Manchester for sulfate, nitrate, ammonium, chloride, calcium, sodium, potassium, magnesium., arsenic, lead, zinc, cadmium, copper and phosphate.

The precipitation in western Washington was found to be acidified (average pH 4.5 to 4.7 at different sites; minimum pH was 3.6), largely by sulfuric acid (65%) and to a lesser extent by nitric acid (35%). Industrial sulfur dioxide emissions are the

probable source of sulfuric acid found in rain. Oxides of nitrogen, largely emitted by autos and trucks are the probable source of nitric acid. We found 65% as much acid was deposited at Bellingham near the Canadian border in comparison to the three sites in and east of Seattle. This could reflect dispersion and removal of pollutants as air moves to the Bellingham site from both the western Washington urban population centers and from the two major sulfur dioxide sources, the ASARCO copper smelter and the Centralia coal fired power plant.

Differences were found between summer and winter precipitation. The concentration of dissolved materials in precipitation was much higher in summer than in winter at all sites and there was much more precipitation per week in winter than in summer. Because of the relation of concentration and rainfall amount, more acid was deposited per week in winter than in summer at Seattle sites. At Tolt and Bellingham, more acid was deposited in summer than in winter because these sites receive much more summer rain than the other two sites. More acid was deposited at Tolt than at any of the other three sites because of the higher rainfall at this site. This indicates that the Cascades probably receive more acid deposition than lowland sites because of their high rainfall.

This study was unable to identify any source or class of sources that cause acid deposition in western Washington by chemical analysis for trace materials emitted by a specific source. Transport, conversion of emissions to sulfuric acid and wash-out of acid in rain was modeled using existing industrial emission data. The model suggests that the major source of sulfuric acid in rain at our three southern sites is the ASARCO smelter.

Acid concentration and deposition in western Washington is generally less than that found in areas where environmental damage has been observed but above the level where researchers have suggested acid rain could cause some environmental impact. The higher lakes in the Cascades are the most sensitive areas in western Washington because these lakes receive high deposition of acid and have little ability to neutralize acid inputs. We suggest continuation of the acid precipitation sampling program and adding measurements of the character of lakes expected to be sensitive and to receive large amounts of acid deposition.

Complete site descriptions are included in the Quality Assurance Plan prepared as part of this program. This QA document and the complete data set of observations is available from the Air Programs Section of U. S. Environmental Protection Agency; Region X; Seattle, Washington.

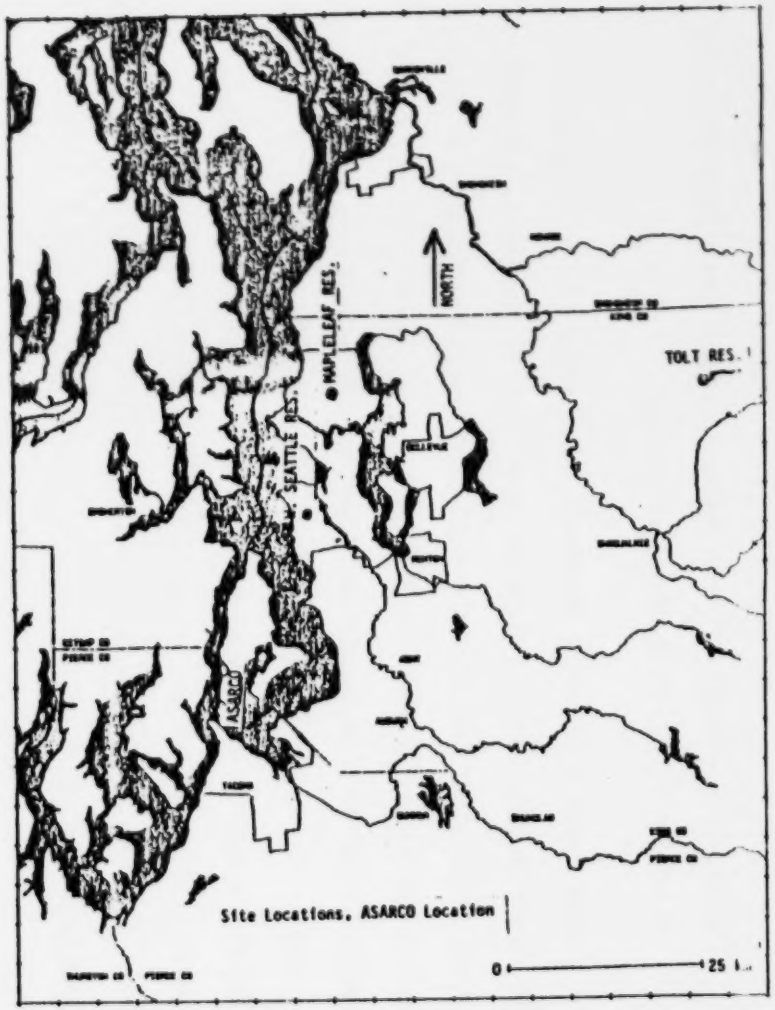


Figure 1. Maps of site locations. Three sites were in and near Seattle as shown above. One site was 2 miles north of Bellingham, shown on the left map. ASARCO's location is shown above.

II Summary of Results from Sampling and Chemical Analysis of Western Washington Precipitation

The data from this program, combined with information concerning the sensitivity of specific biological systems to acid deposition, can be used to estimate the potential for damage by emissions of acid forming pollutants in this region. This estimate of damage could be used to guide future emissions policy in which the advantages of industrial production will be balanced against cost of emission control and environmental impacts. Impacts are estimated by comparing current character of precipitation in this region to that in areas with reported damage from acid deposition.

Previous investigators have reported acid rainfall in western Washington (Larson et al., 1975; Logan et al., 1982) with substantial concentrations of sulfate and nitrate associated with acidity of rainwater. We find that sulfate and nitrate account for essentially all of the acidity in sampled rain with sulfate supplying 75% in Seattle and 65% at Tolt and Bellingham. For the average weekly sample, acid species are partially neutralized by ammonium (13 - 22%) and by calcium (9 - 16%) compunds.

Evans et al., (1981) and Glass et al., (1981) have suggested that an annual rain volume weighted pH of less than 4.6 and/or annual deposition above 1.5 gram of sulfate (SO_4) per square merter are the thresholds for effects of acid deposition on fish populations. We found that Western Washington received acidic rainfall in 1982 -1983 with an annual volume weigted pH of 4.4 to 4.5 in Seattle and 4.6 at Tolt and Bellingham. The measured

SO_4 annual deposition was 1.3 g/m² in Seattle, 1.7 g/m² at Tolt and about 0.9 g/m² at Bellingham (Bellingham deposition was measured to be 0.7 g/m² in 42 weeks). The measured values of mean pH and sulfate deposition are at or above the threshold of damage to fish populations in sensitive lakes.

Failure of fish populations to reproduce have been reported from high acid deposition areas such as NE United States, eastern Canada and southern Sweden (EPA, 1982). Annual deposition of SO_4 is higher in New Hampshire and southern Sweden (2 to 5 g/m²) than we have measured in western Washington (0.9 to 1.7 g/m²). (SO_4 from sea salt has been subtrtacted from these deposition values.) The pH in western Washington averaged about 4.5, less acid than the pH of 4.3 reported in Sweden and 4.13 reported in New Hampshire. The acidity of western Washington rainwater is due to the small concentrations of neutralizing species such as ammonium and calcium as well as to the acid associated with sulfate and nitrate. Western Washington rain is characterized by its low concentration of dissolved ions as indicated by the volume weighted conductivities of 10 uS/cm (micro-Seimens per centimeter) in Bellingham and Tolt and 15 uS/cm in Seattle. In Sweden the conductivity averaged 28 uS/cm. Sea salt spray and soil materials contribute to the precipitation conductivity in western Washington.

Added data on lake buffering capacity (ability to neutralize acid input) and acid input is needed to predict impacts on specific lakes. Specific forest tree species in north-eastern US appear to be damaged by levels of acid deposition several times

higher than we have found here. Acid fog, probably not found here, may have a role in creating these forest impacts in the northeastern United States. Effects of acid precipitation on farm productivity have been studied by others and they have reported some crop yields are increased and some decreased by acid deposition.

This study has found that rainfall in western Washington is less acid and that less sulfate is deposited than in rain found in areas with reported damage to fish and forest productivity. We appear to be above the threshold level of acid precipitation damage, but our rain is substantially below the levels of acidity associated with obvious damage to fish and forest productivity. Measured deposition levels are high enough to expect some damage. Damage will be first found in sensitive lakes and in sensitive forest systems located in regions of high acid deposition. Some regions of western Washington, especially the higher Cascades, are sensitive to acid deposition because the watersheds surrounding these lakes are low in capacity to neutralize acid inputs. The soils in the Cascades have some similarity to the soil types found to be associated with acid impact on forest productivity. Additional studies are needed to determine the sensitivity of lakes to acid input, the sensitivity of species populating the lakes and the amount of acid deposited in the lakes. To guide emission control policy, additional information is needed relating emissions by spetific sources to acid deposition.

III Chemical Composition of Western Washington Rain

Local sources may alter the chemical composition of precipitation. Sites were chosen to represent regional rather than local sources to characterize the regional character of Western Washington precipitation. All of the samplers in this study except for the site at University of Washington were located in grassy, dust free areas in an attempt to avoid altering rainwater chemistry by interaction with the chemistry of local soil dust. Sites were chosen for this study to detect effects of transport wind direction, regional pollution sources and estimate effects of wet deposition on specific locations.

The 1000-2000 foot level winds are representative of the planetary boundary layer where transport of sulfur and nitrogen pollutants takes place. Three years data collected at Portage Bay (in North Seattle) by Washington State Department of Ecology and six years data collected at Sea-Tac airport by NOAA indicate that south to southwesterly aloft winds occur 75 percent or more of days with rainfall. Figure 2 presents the winds at Sea-Tac for days with rainfall in 1956-61 (Vong, 1982). Accordingly, the sites for sample collection are oriented to the general North-Northeast direction in order that during rainfall they will be downwind of the urban Seattle SO_2 and NO_x emissions and the major sulfur dioxide emission sources in Tacoma and at Centralia (Puget Sound Air Pollution Control Agency, 1983). Limited aloft wind data collected at Portage Bay during this 1982-83 sampling period confirm that the prevailing aloft wind direction for days with rain is from the south-southwest. Of 23

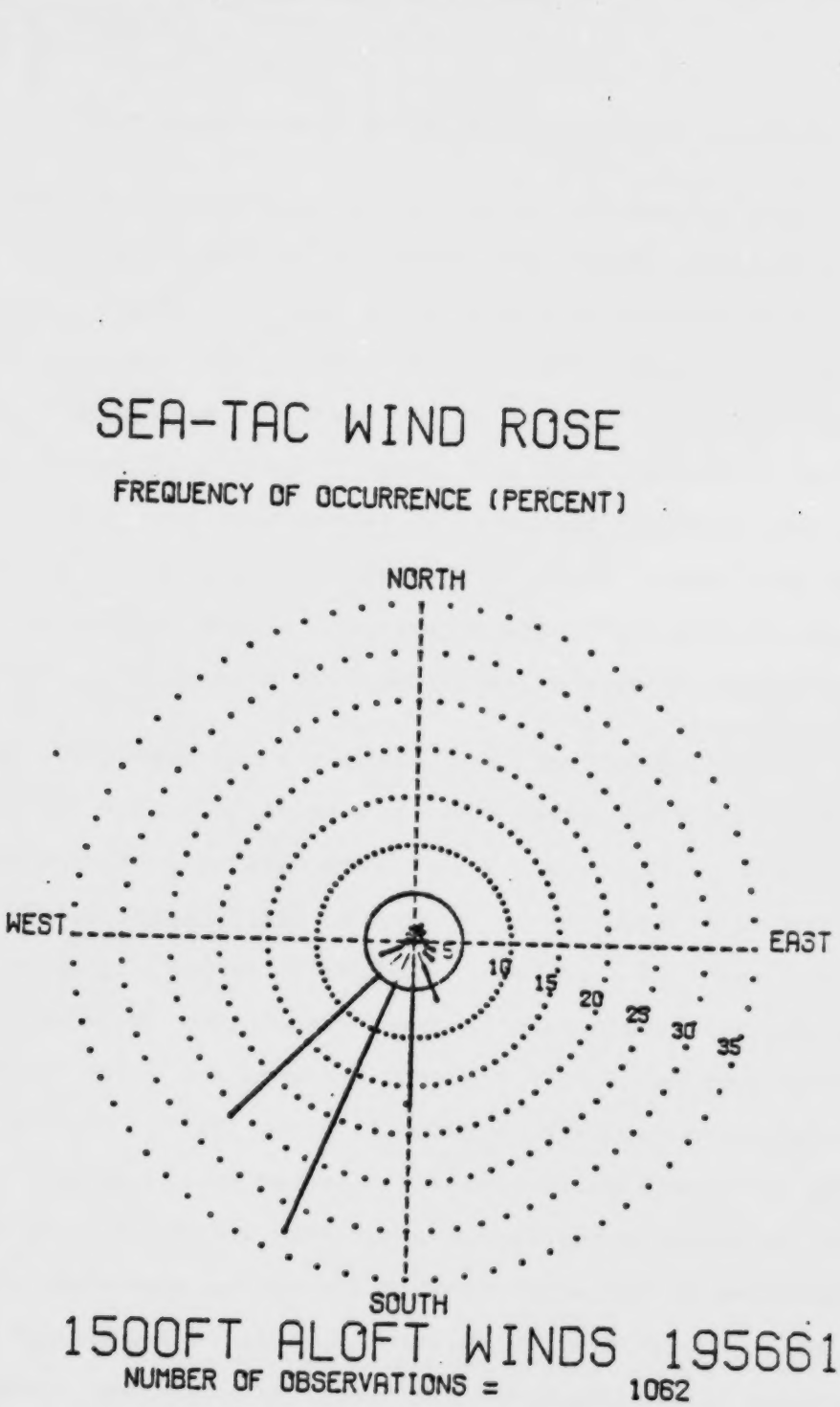


FIGURE 2 :

Seattle-Tacoma Airport 1500 foot aloft winds for rain days.

rainy days of aloft wind observations in 1982 - 1983, 15 show winds from the S to SW sectors indicating that under usual rain conditions, pollutant transport in Puget sound is toward the north and east and toward the Cascade Mountains.

Samples of precipitation were collected in the Wet - Dry type of precipitation sampler used in the NADP national rain sampling network. A detector is used to activate a motor driven lid to open the wet collection bucket to rainfall. Wet deposition falls into one plastic, acid washed bucket and the liquid sample was collected at weekly intervals, as specified by NADP. The sample bucket was replaced with an acid-washed bucket that has been rinsed with distilled, deionized water. The rinse water was analysed to detect contamination. The conductivity and volume were measured at the sampling site and the sample transported to the University of Washington. After 24 hours, the sample conductivity and pH were measured and the sample sent to the EPA Laboratory at Manchester, WA.

Sulfate, nitrate, chloride and ammonium ion concentrations were measured as first priority, then other ionic species, pH and conductivity. Species analyzed were selected to provide information on the chemical makeup of rain and the sources of these contaminants. Chemical analysis provided concentrations of the following species: arsenic, lead, zinc, cadmium, copper, phosphate, sulfate, nitrate, chloride, sodium, potassium, magnesium and calcium. Conductivity and pH were measured both in the field and in the lab when there was sufficient sample volume.

The effect of sea salt on precipitation composition can be detected and subtracted from measured concentrations because the concentration of major ions in sea water are in a constant ratio, assuming no fractionation occurs (Junge. 1963). Assuming that sea salt is the only emission source for chloride, the remaining contribution of sodium, magnesium, calcium, potassium, and sulfate by sea salt can be calculated from known sea salt ionic concentration ratios to chloride (Holland, 1978). The concentration of listed ions after sea salt contribution is subtracted is referred to as "excess". Other investigators have used sodium or chloride for calculation of excess. If there are no other sources of sodium or chloride the ratio of Cl/Na in precipitation should be 1.8. In this region, the ratio of Cl/Na is close to 1.8, indicating that most of these two ions come from the sea. This study found a small deficit of sodium as indicated by the negative excess sodium (data in Appendix C). If sodium had been used to correct for contributions from sea salt aerosol, the excess sulfate and calcium would all slightly increase over their excess concentrations based on chloride. Table 1 lists measured concentrations and depositions. Figures 3 and 4 present

cumulative deposition of four major ions. Excess sulfate is generally used as a measure of deposition because this removes the ions from sea salt which is a relatively local, natural source of sulfate. Excess sulfate is a measure of the impact of man on rainwater composition (assuming negligible biological and volcanic sources of sulfur emissions, an assumption that appears reasonable for this area, except during periods of high volcanic sulfur emission).

TABLE 1

Northwest Rain Chemistry Measurements: February 14, 1982 - February 15, 1983

Summary of Data : Weekly Volume, Deposition, and Volume Weighted Mean Concentrations and (Standard Deviation)

Site	West Seattle	Maple Leaf	Tolt Reservoir	Bellingham
Sum, (+/-)	1.17 (.29)	1.15 (.22)	1.21 (.40)	1.19 (.29)
NO_3/SO_4 (Molar)	0.63 (.29)	0.72 (.30)	1.06 (.72)	1.07 (.46)
Volume (ml)	1221	1236	2670	1067
Rain (mm)	19.2 (24.3)	19.4 (21.4)	42.0 (37.9)	16.8(27.2)
pH (field)	4.44	4.41	4.60	4.57
Lab Cond. (uS/cm)	15.6 (6.6)	15.3 (6.5)	9.9 (7.0)	10.3 (5.9)
Lab pH (from regression)	4.53	4.51	4.66	4.64
# of Weeks with Zero rain	8of52	6of52	4of52	7of44
	Deposition, g Per Square Meter Per Year			
SO_4 (excess)	1.34 (1.6)	1.29 (1.1)	1.65(1.4)	0.73(0.43)*
H^+	0.036 (.42)	0.039 (.58)	0.036(.51)	0.019 (.29)*
NO_3 as N	0.10 (.1)	0.12 (.1)	0.21 (.18)	0.1 (.1)*
NH_4 as N	0.06 (.07)	0.08 (.08)	0.11 (.1)	0.07 (.06)*

*Deposition in 42 weeks at Bellingham.

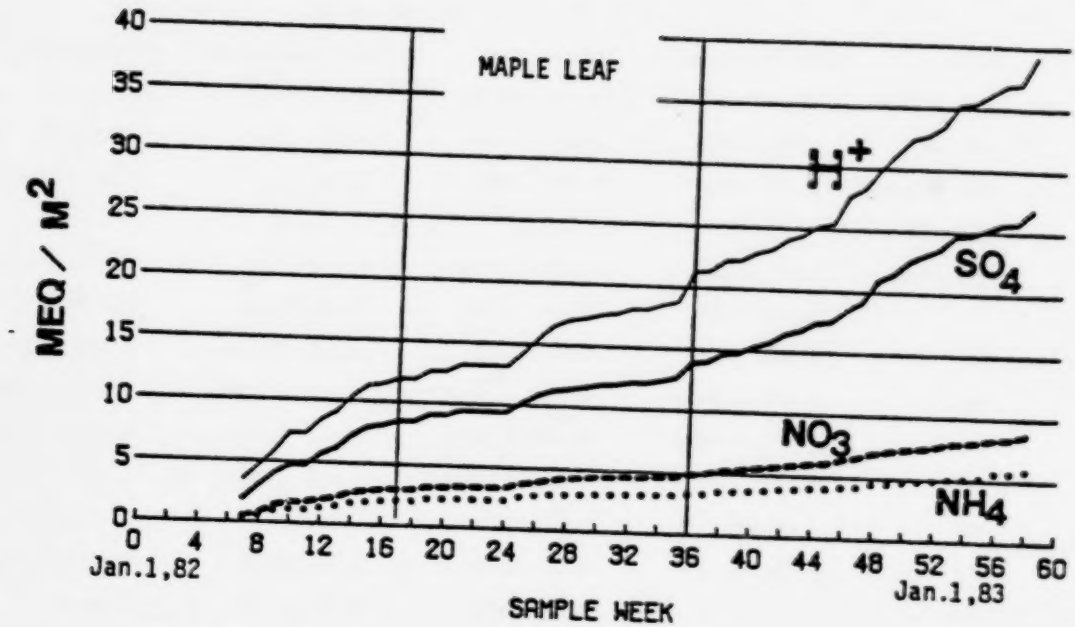
TABLE 1, Continued

Northwest Rain Chemistry Measurements: February 14, 1982 - February 15, 1983

Concentrations, mg Per Liter

Site	West Seattle	Maple Leaf	Tolt Reservoir	Bellingham
H+ (ug/l)	36.42 (23.4)	38.76 (24.2)	25.53 (24.0)	26.90 (22.3)
NH_4 as N	.064 (.05)	.081 (.09)	.052 (.06)	.075 (.07)
SO_4 (Excess)	1.34 (.83)	1.27 (.78)	0.76 (.61)	0.83 (.56)
SO_4 (Total)	1.42	1.33	0.82	0.89
NO_3 as N	0.101 (.073)	0.121 (.102)	0.100(.103)	0.113(.096)
Cl	0.584 (.63)	0.441 (.43)	0.405 (.32)	0.408 (.42)
Na	0.265 (.32)	0.219 (.22)	0.222 (.19)	0.225 (.20)
Mg	0.042 (.045)	0.033 (.040)	0.034 (.025)	0.031 (.028)
Ca	0.128 (.173)	0.098 (.103)	0.045 (.023)	0.052 (.039)
K#	0.027 (.031)	0.026 (.036)	0.028 (.031)	0.037 (.042)
PO_4	<0.002	<0.002	<0.002	<0.002
Pb (ug/l)	3.54 (4.1)	5.00 (6.6)	1.83 (2.6)	1.52 (2.1)
As# (ug/l)	3.18 (4.6)	2.21 (2.8)	1.15 (2.3)	0.56 (1.4)
Cu# (ug/l)	4.47 (4.7)	5.07 (5.5)	1.86 (3.6)	2.09 (4.7)
Zn# (ug/l)	5.56 (5.7)	4.57 (6.3)	1.85 (3.0)	5.13 (22.7)
Cd# (ug/l)	0.33 (0.72)	0.43 (2.3)	0.87 (2.9)	0.10 (0.26)

#This data should be used with caution. The concentrations of these ions are detection limits.



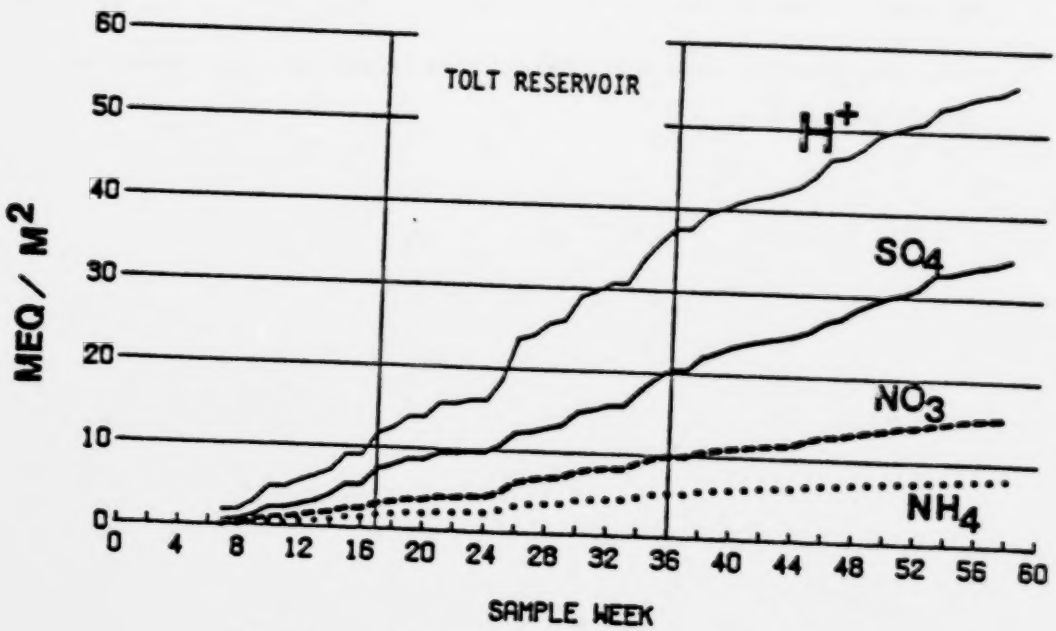
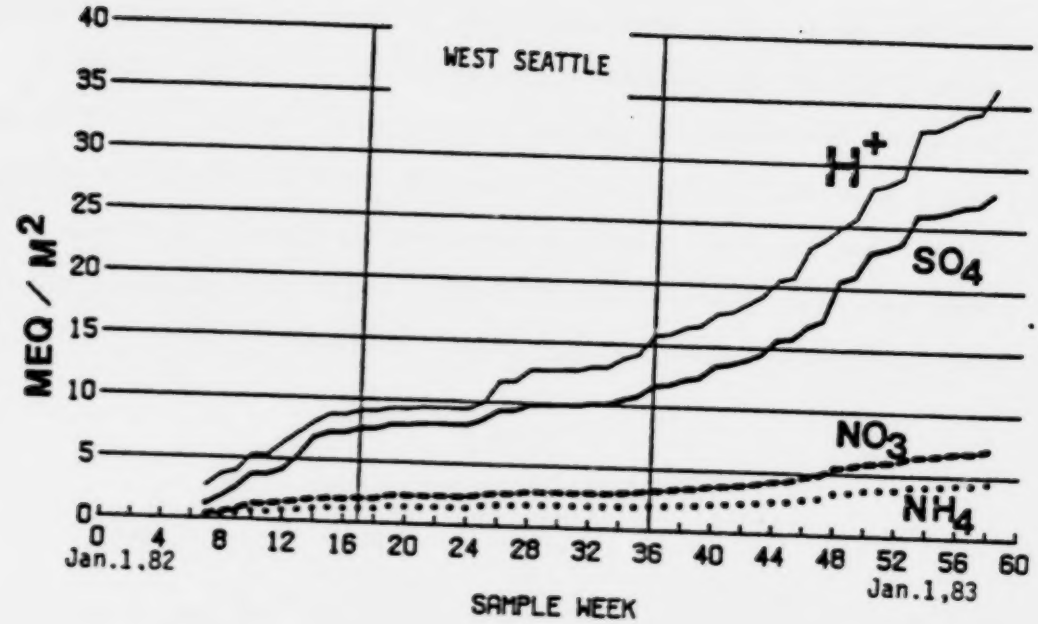


FIGURE 3 : Cumulative Deposition of Major Ions



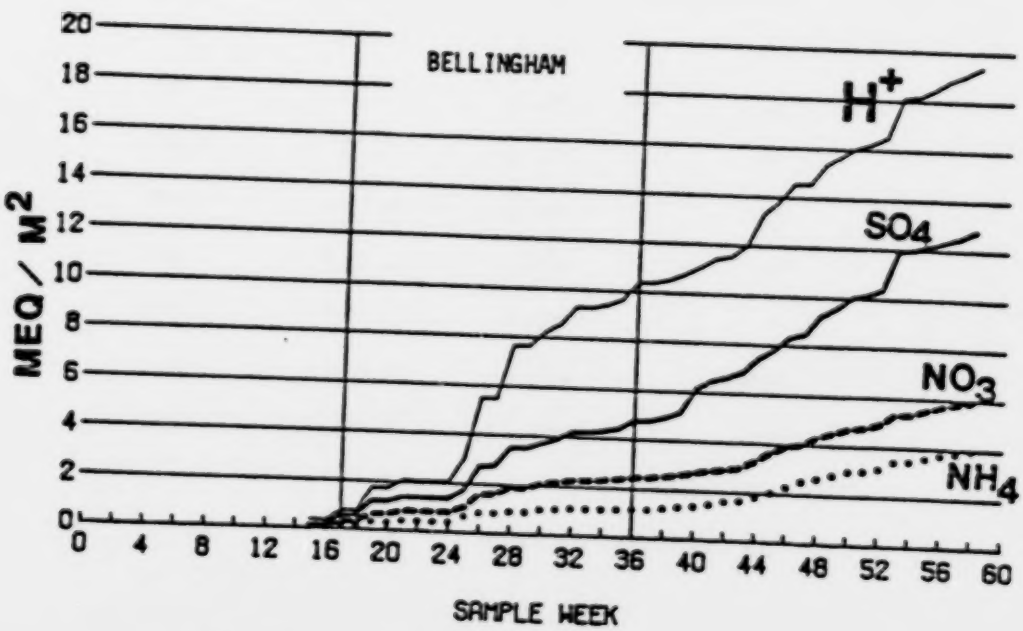


FIGURE 4 : Cumulative Deposition of Major Ions

The observed rainwater composition reflects its initial background composition plus the added species from polluted air. To detect effects of added pollutants on precipitation quality, we have compared rainwater data collected at the Hoh River Ranger Station, Olympic National Park to measurements of this program. The Hoh River data were collected as part of the NADP network and were analyzed at the NADP laboratory in Illinois. Table 2 presents Hoh River volume weighted concentrations for 9 major ionic species. Trace metal analyses (trace metals are those other than Na, Mg, Ca and K) were not performed on these samples. Two years (July 1980-July 1982) of rainwater are represented and used as background values.

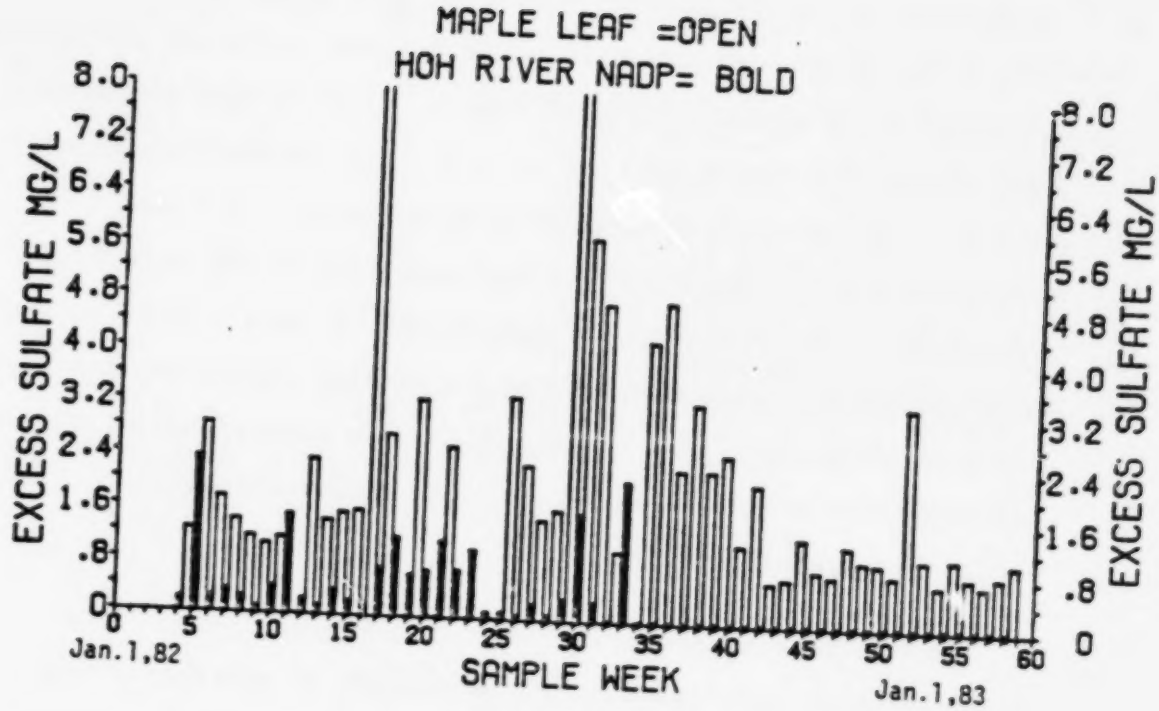
TABLE 2

Hoh River NADP Rainwater Data
(July 1980-July 1982, weekly wet samples)
Volume weighted mean (Standard deviation)

Rainfall	mm/wk	65	
SO_4(total)	mg/l	0.41	(.28)
SO_4(excess)	mg/l	0.22	(.18)
NO_3	mg/l	0.091	(.09)
Cl	mg/l	1.36	(1.55)
Na	mg/l	0.72	(.80)
Mg	mg/l	0.090	(.09)
Ca	mg/l	0.062	(.09)
K	mg/l	0.033	(.03)
NH_4	mg/l	0.005	(.01)
H+	ueq/l	4.06	(1.56)
pH(laboratory)		5.39	
Conductivity	uS/cm	8.69	(6.2)

Hoh River data and this study overlap by 19 weeks and are presented graphically in Figures 5-6 for comparison of the concentrations in Seattle. We assume that Hoh precipitation is not affected by anthropogenic emissions and represent background precipitation quality for this region. The nitrate and excess sulfate at the Hoh River have similar time variability when compared to the data collected in Puget Sound, perhaps invalidating our assumption or perhaps showing the effect of variable rainfall altering concentration of both backgound and anthropogenic contaminants. The background values are subtracted from our measured ionic concentration and deposition values to estimate the effect of sources in the industrialized and urbanized Western Washington.

Hoh River site precipitation has 2.5 times higher salt concentration than Seattle rain and about 17 percent of the average excess sulfate and 18 percent of the average nitrate concentration in Seattle. Other investigators have reported remote sulfate concentrations which are consistent with these data from the Hoh River NADP site (Galloway, 1982). Ammonium and excess cation concentrations at the Hoh River are near zero. Since transport distance for sea salt particles is limited (due to the large size of particles), the sea salt is considered to be a local influence on rain composition. Our use of Hoh River data does not attempt to distinguish between natural sources and transport of distant anthropogenic emissions, both of which could contribute to Hoh River rainwater quality.



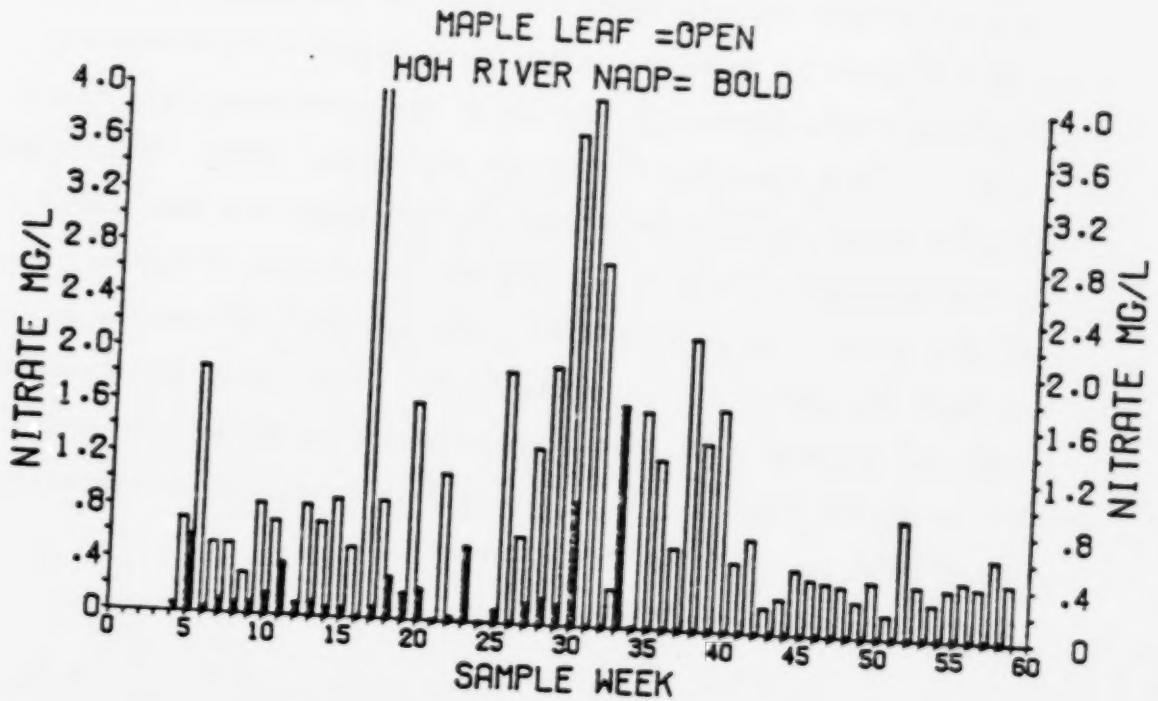
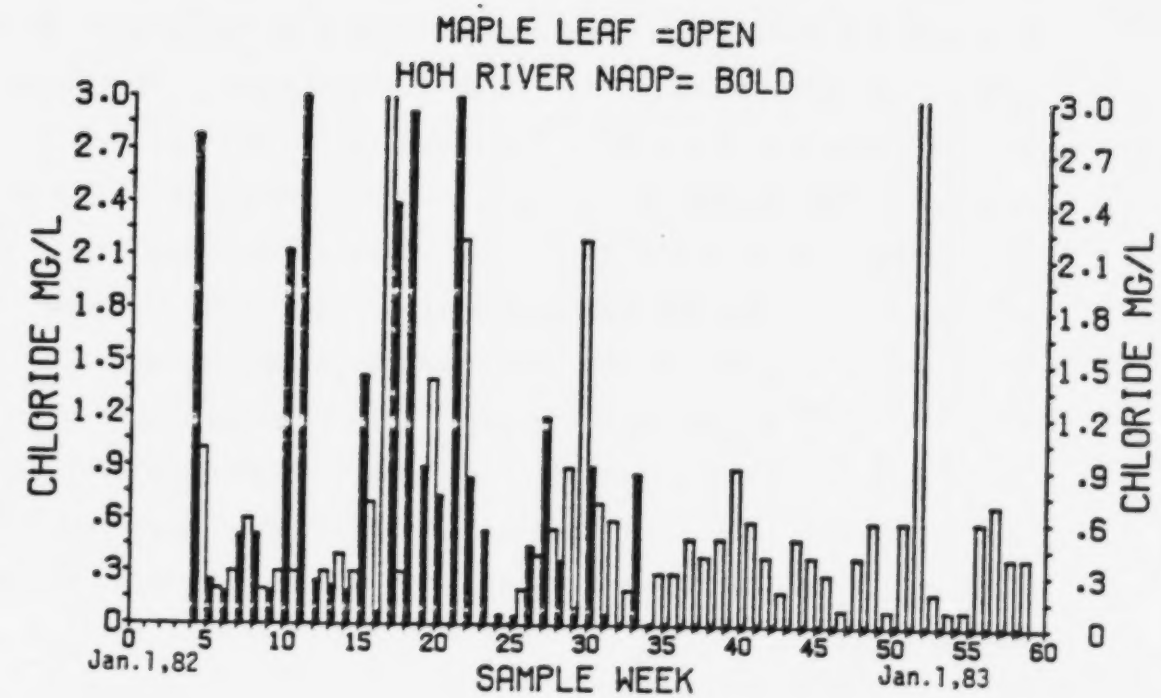


FIGURE 5 : Weekly Concentration



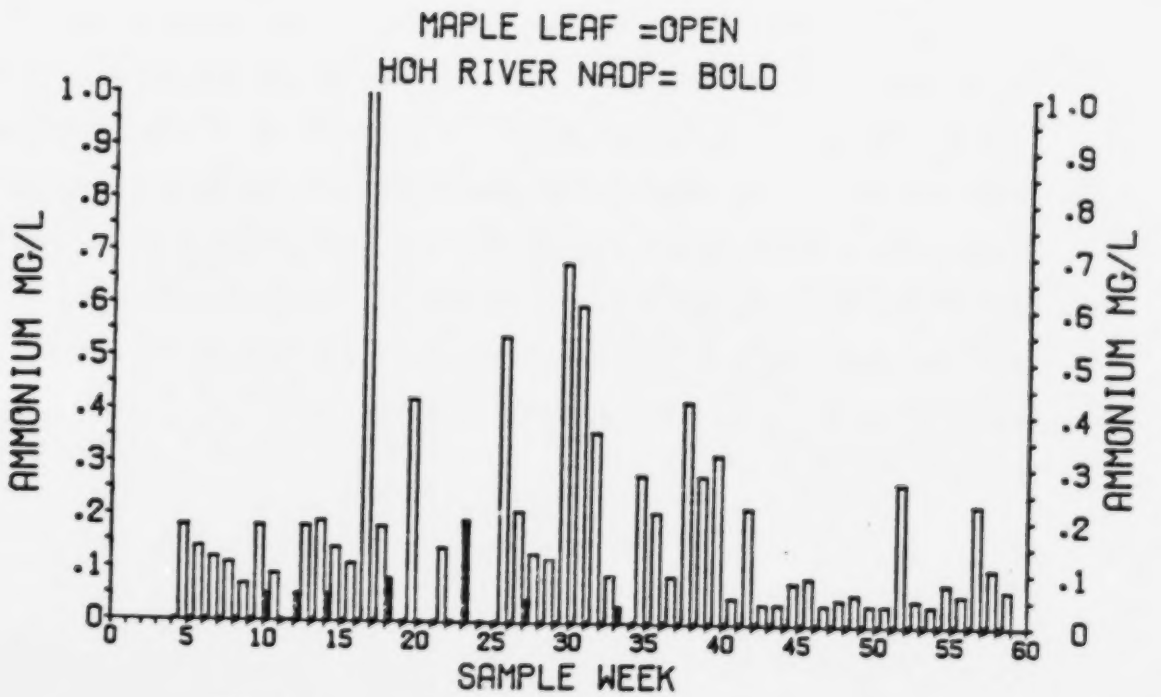


FIGURE 6 : Weekly Concentration

The 204 weekly rainwater samples collected in this program have been analyzed for correlations within these data. Appendix B presents the correlation coefficients by sampling site. Hydrogen ion correlates with excess sulfate at Maple Leaf (R = 0.81), the Tolt Reservoir (R = 0.88), Bellingham (R = 0.67) and West Seattle (R = 0.60). Hydrogen ion correlates with nitrate at Maple Leaf (R = 0.75), the Tolt Reservoir (R = 0.90), and in Bellingham (R = 0.78). This supports the idea that sulfate and nitrate are the anions which donate the hydrogen ion in rainwater in Washington. The correlation of NO_3 and NH_4 is R = 0.78 or higher at all sites. Lead concentration is correlated with nitrate at all locations sampled (R = 0.61 to 0.72) and with sulfate in Seattle and at the Tolt Reservoir (R = 0.57 to 0.73). All concentrations are negatively correlated with rainfall volume.

Sea salt species contribute a third relationship to the chemical composition of Western Washington wet deposition. The chloride correlation with sodium and magnesium ranges from R = .80 to .95 at all sites studied. Figures 7, 8, 9 and 10 present time series of the equivalent concentrations of these species for each site. These plots illustrate the higher concentrations that occur for low rainfall, summer samples. Species have been grouped according to the correlations discussed above and as identified by multi-variate analysis.

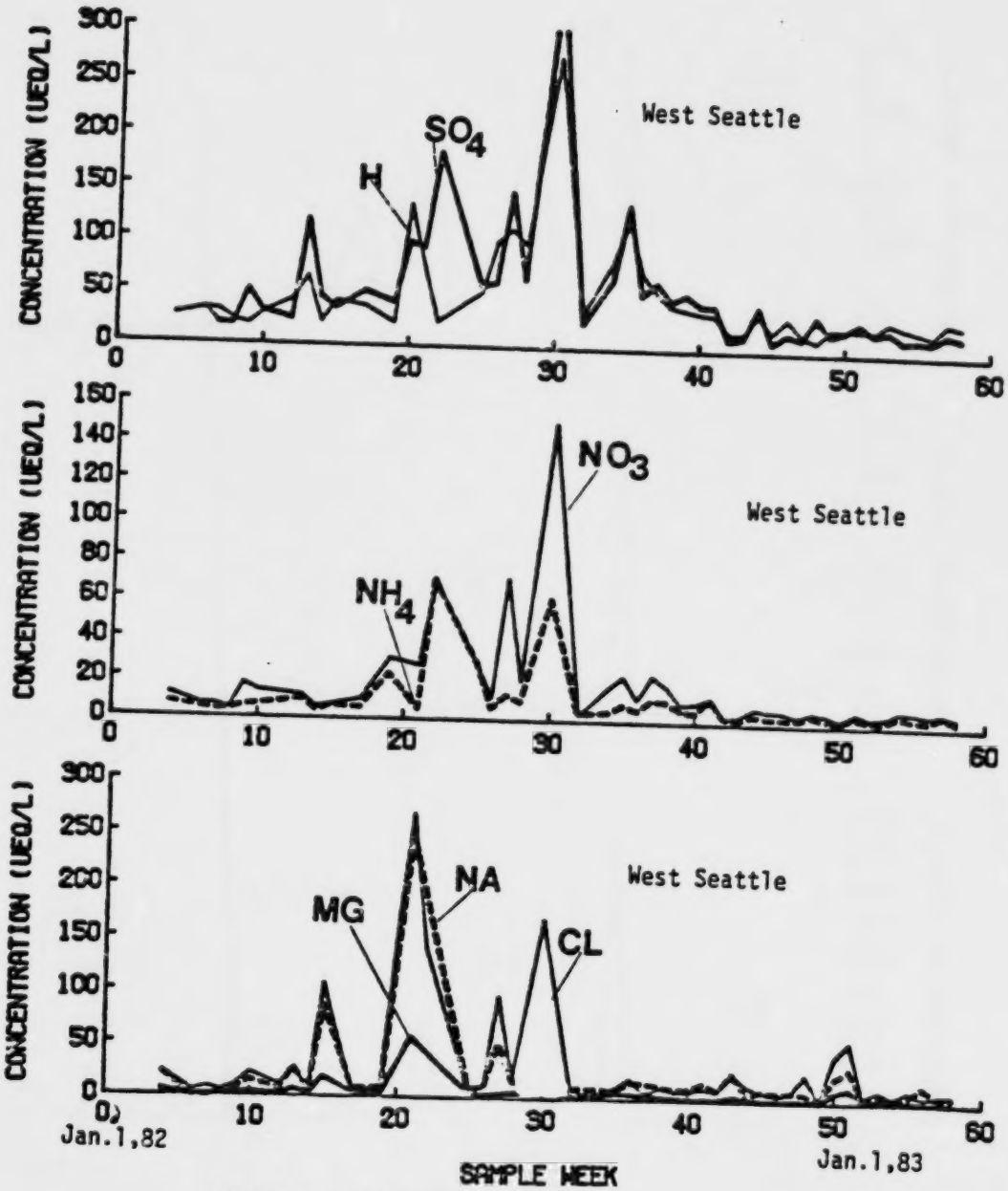


FIGURE 7 : Weekly Concentration

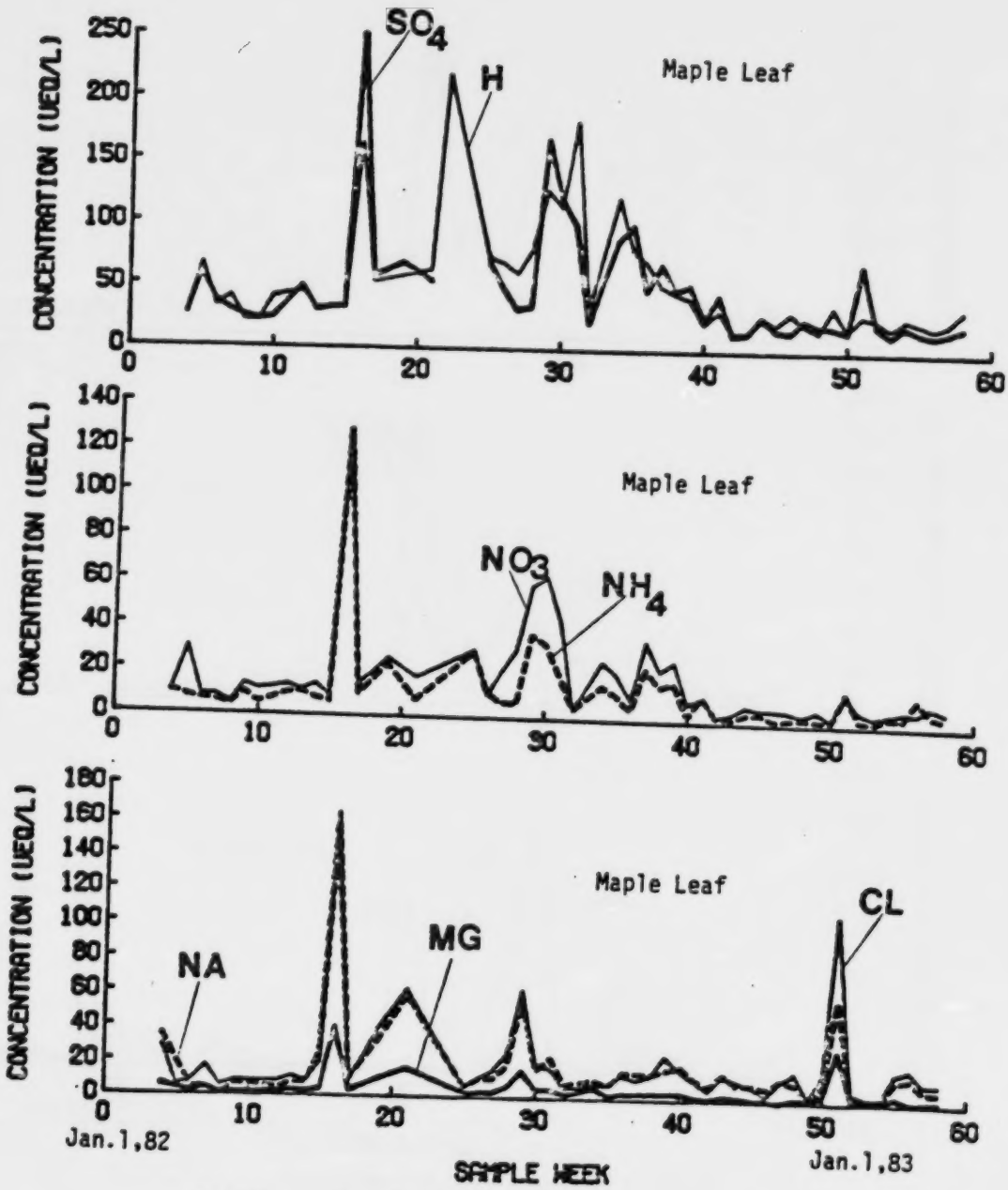


FIGURE 8 : Weekly Concentration

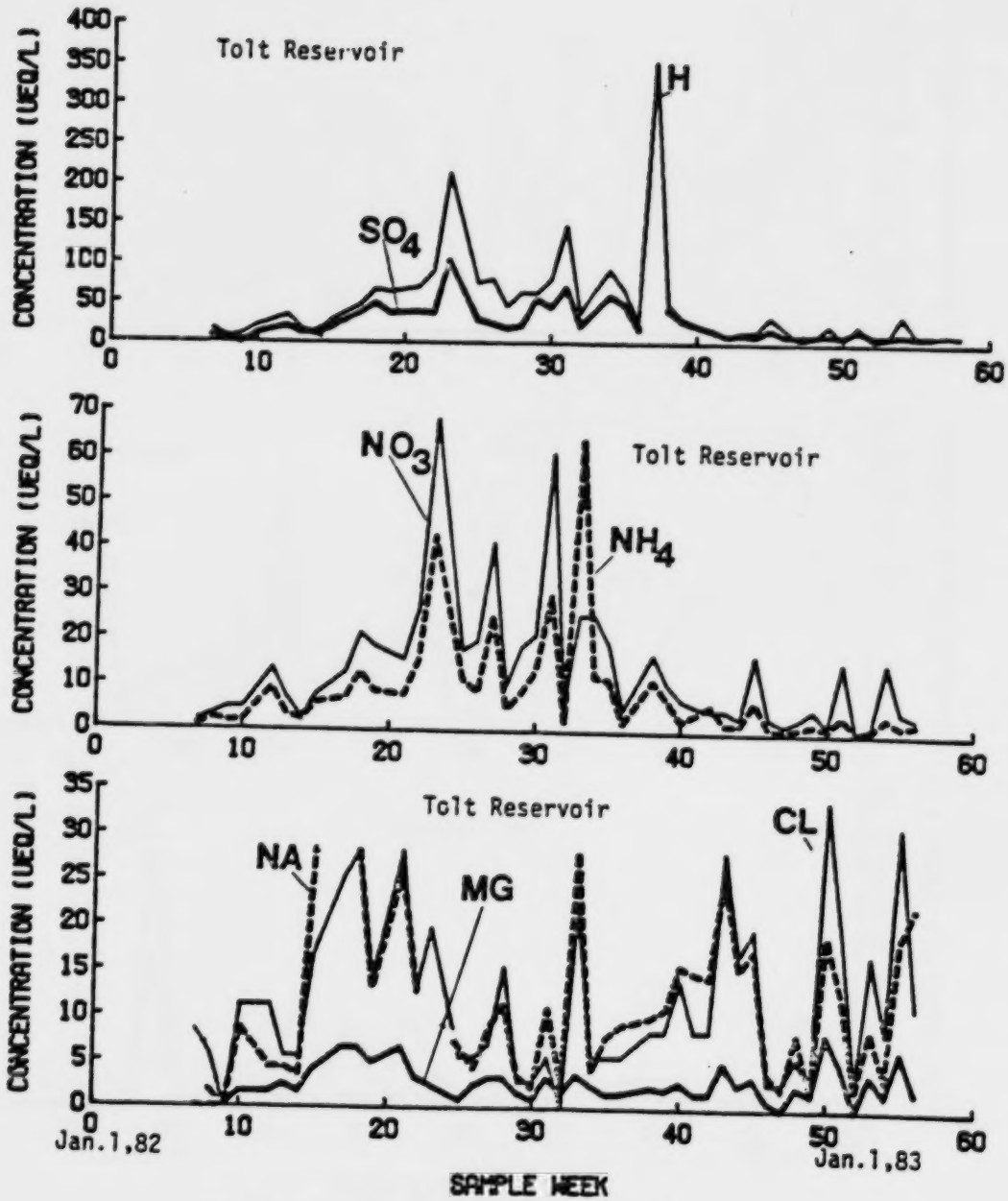


FIGURE 9 : Weekly Concentration

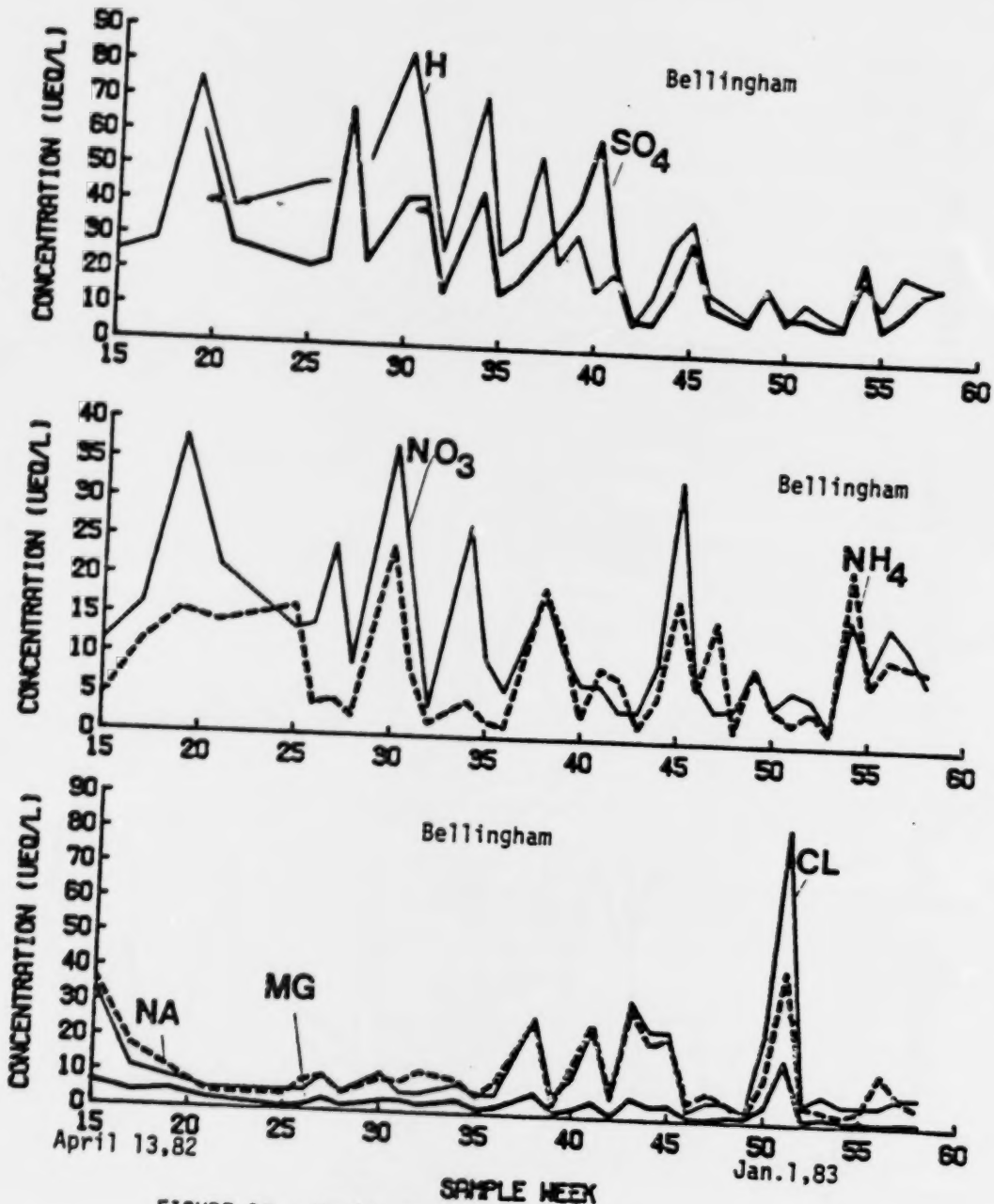


FIGURE 10 : Weekly Concentration

The multiple correlations of chemical composition have been examined using a statistical program available at the University of Washington, SPSS, for factor analysis. This program examines the entire data set for mutual tendencies of variability in chemical makeup. Factors are then computed which can be used to help identify sources of variability in rainwater composition. Factor analysis detected the following groupings in the data:

TABLE 3
Grouping Identified BY Factor Analysis

Site	Factor 1	Factor 2	Factor 3	Factor 4
Bellingham	Cl, Mg, Na	NH_4, NO_3	Pb#	H+, NO_3 SO_4
West Seattle	Cl, Mg, Na	NH_4, NO_3	As#, Pb#	H+, SO_4
Maple Leaf	H+, NH_4,	Cl, Mg, Na	As#, Pb#, Ca	- - - -
Tolt	H+, NH_4, Pb# NO_3, SO_4, Ca	Cl, Mg, Na	- - - -	- - - -

#Pb and As are of low accuracy because of low concentrations in precipitation.

Note that several factors (likely to be specific sources) have been identified by this analysis. These include sea salt (Na, Cl, Mg) and sources related to man (H+, NH_4, As, Pb, NO_3, SO_4). Within the last factor, different combinations are detected at different sites. We found similar results for factor analysis performed using both excess and total cation concentrations and deposition.

Spatial Variability of Seattle Rain Composition

Rainwater composition within the Seattle area was examined to detect effects of non-uniform emissions and transport of pollutants in the city. Two or three rain collectors were operated at different locations in Metropolitan Seattle. For the period, April 27 - September 7, 1982 a sampler was operated at the Universiy of Washington, on the roof of Wilcox Hall.

TABLE 4
Comparison of Seattle Collection Site Locations
Rainwater Composition, Summer (April 27-September 7, 1982)
Volume Weighted Mean Concentrations, mg/l

Site	U. of Wash.	Maple Leaf	West Seattle
SO_4 (Total)	4.31	2.73	2.84
SO_4 (Excess)	4.17	2.64	2.77
NO_3 as N	0.43	0.29	0.26
NH_4 as N	.28	.20	.17
Cl	.97	.67	.53
Na*	.48	.40	.34
Mg*	.09	.07	.06
Ca	.52	.18	.32
K#	.09	.08	.08
Pb* (ug/l)	17.3	11.3	8.9
As# (ug/l)	2.3	1.6	2.0
Zn# (ug/l)	9.7	5.3	5.5
Cd# (ug/l)	1.7	0.7	0.4
Cu# (ug/l)	6.1	5.5	5.7

*Some missing samples because volume insufficient for measurement.

#Values of questionable accuracy because low concentrations of these ions are near detection limit.

TABLE 4, CONTINUED
Comparison of Seattle Collection Site Locations
and Rainwater Composition

19 Weekly Samples Taken in Summer (April 27-September 7, 1982)

Site	U. of Wash.	Maple Leaf	West Seattle
Sum, (+/-)	1.07	1.21	1.28
NO_3/SO_4 (Molar ratio)	.37	.40	.34
Summer Deposition in quantity/M^2 Per Week			
S dep (mg)	5.97	3.77	3.04
H (meq)	.40	.38	.29
NO_3 as N (mg)	1.85	1.26	.85
NH_4 as N (mg)	1.22	.86	.56
Average Summer Values			
H+ (field, ueq/l)	93.3	89.5	87.9
pH (field)	4.03	4.05	4.06
Conductivity	35.0	25.6	23.0
Average Volume (ml)	288	273	209
Rainrate (mm/wk)	4.5	4.3	3.3
Weeks with rain	14	14	13
Weeks, no rain	5	5	6

Conclusions from Table 4

1) pH varies only slightly between the 3 locations.

2) Weekly Rainfall Volume was variable between sites within Seattle, especially in the summer.

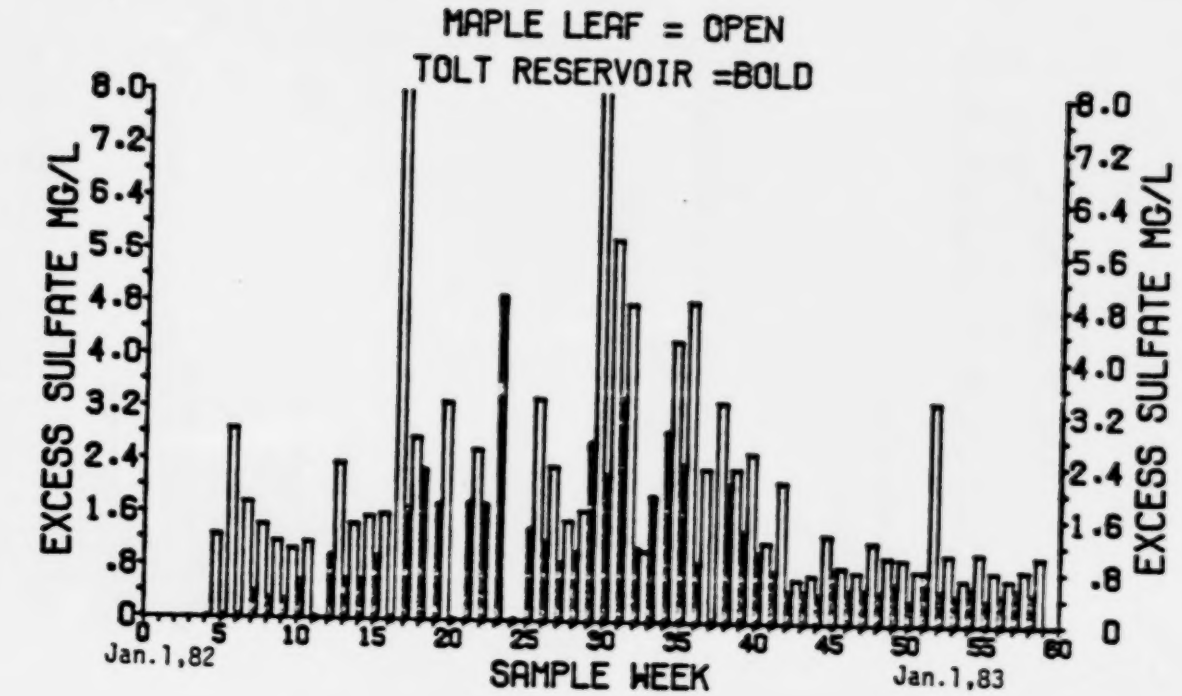
3) Deposition is highest for all ions at the University of Washington.

The similarity in pH at University of Washington and Maple Leaf dispite quite different concentrations of excess SO_4, and NO_3 suggests that some of the additional sulfate at University of Washington may be in the form of calcium sulfate. The observed elevation of lead and nitrate concentrations was expected at the University of Washington site because of proximity to the University district auto traffic. The presence of additional sea salt, calcium, sulfate and nitrate at University of Washington explains the higher conductivity (35 uS/cm compared to 23-25 at other Seattle sites) at University of Washington. Similar pH indicates added NH_4 neutralized the higher nitric acid concentrations which were measured for summer rainfall at University of Washington when compared to the two other Seattle sites.

These results illustrate effects of localized pollution sources as site variability of collected rainwater composition. To characterize rainfall quality for an entire region and not just a local area, sites should be as free as possible from local influences.

Comparison of Tolt Reservoir and Seattle Rainwater

Figures 11-13 present concentrations of 5 species for the sampling period for the Tolt Reservoir sampling site in the Cascade foothills South of Stevens Pass and for Maple Leaf reservoir in Northern Seattle. The Tolt site receives lower concentrations of all species except cadmium. Comparison of correlations in these chemical data indicate that Tolt Reservoir rainwater may be influenced by the same source



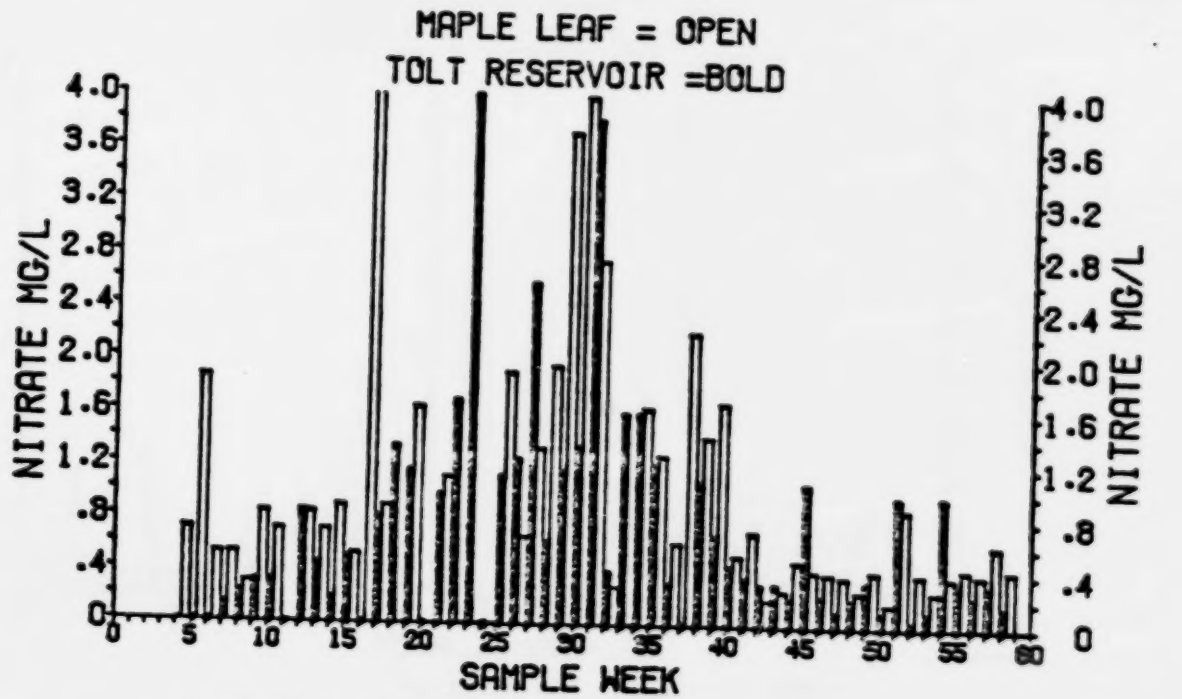
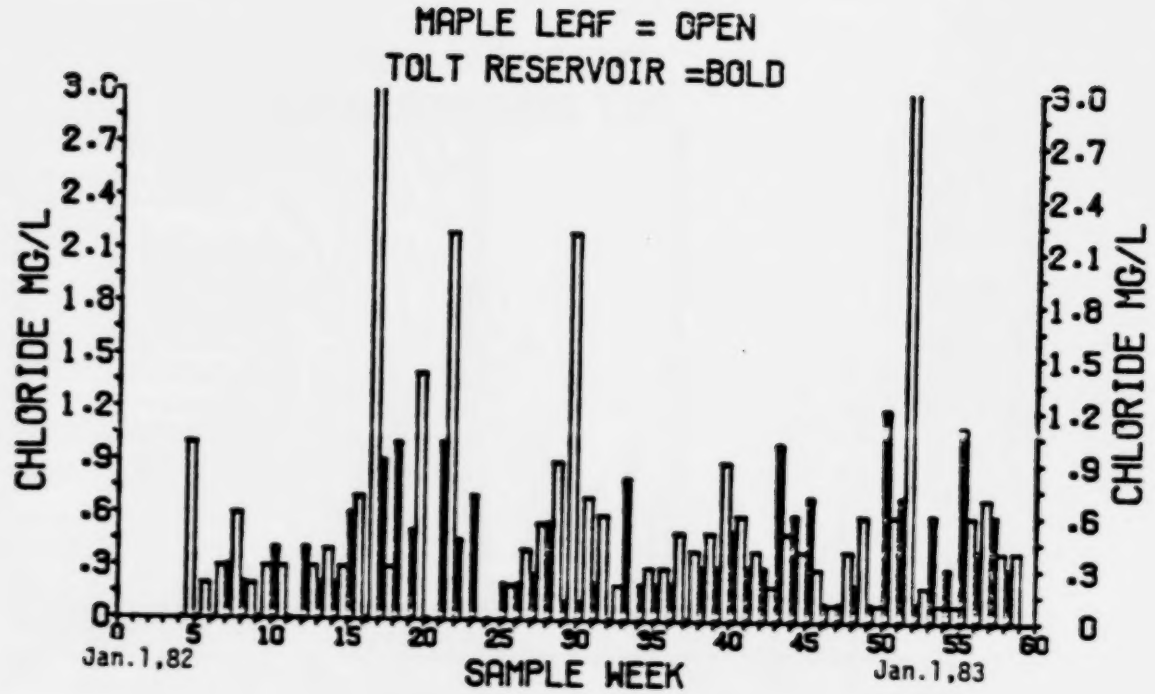


FIGURE 11 : Weekly Concentration



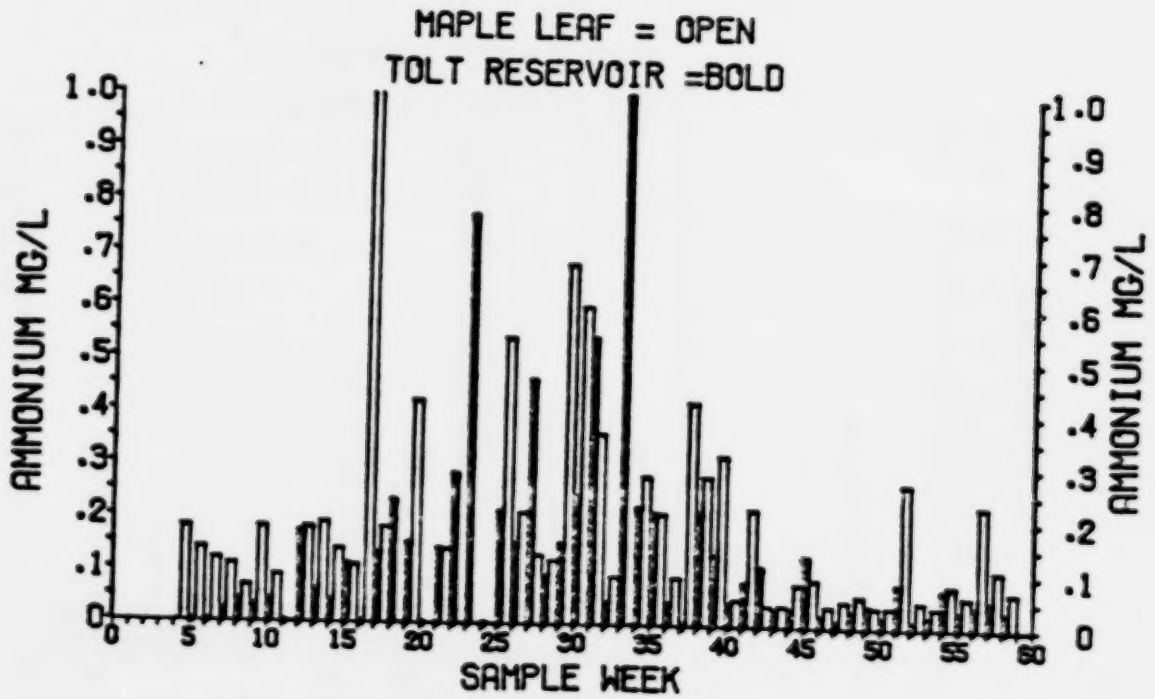


FIGURE 12 : Weekly Concentration

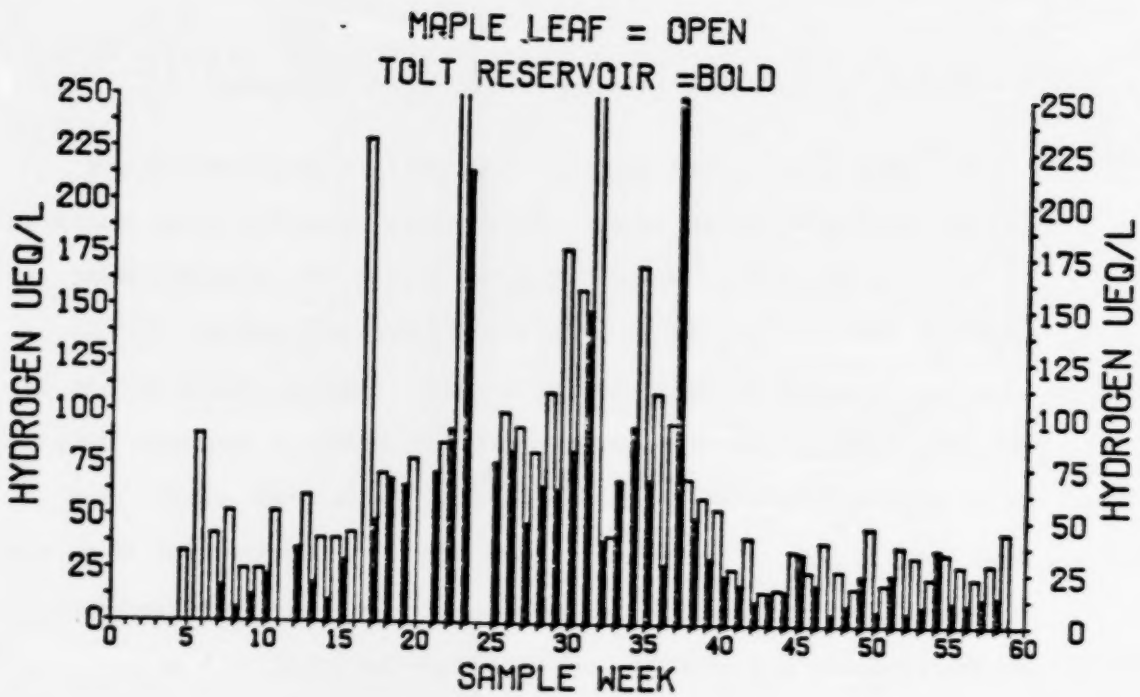
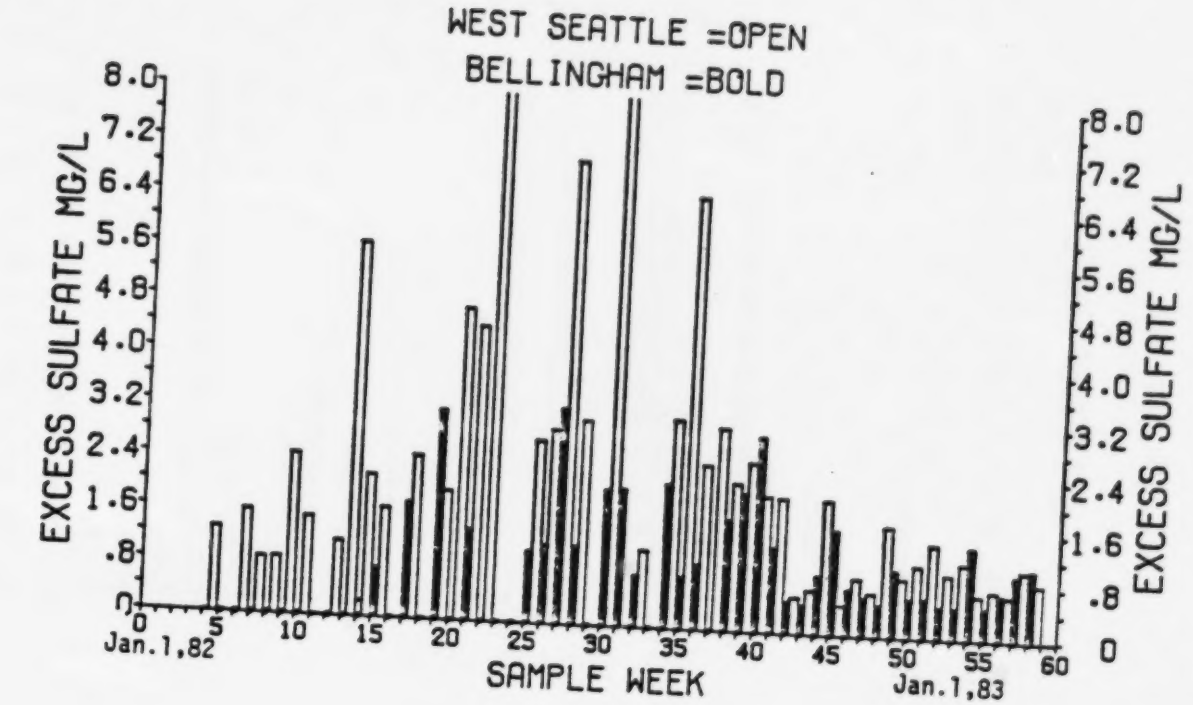


Figure 13: Weekly Concentration

factors as North Seattle but experiences lower concentrations due to dilution of airborne material and by topographically forced higher rainfall rates (Maple Leaf elevation, 50 meters; Tolt elevation, 538 meters). Factor analysis indicates that variability at both Maple Leaf and Tolt is dominated by two sources, industrial-auto and by sea salt. In contrast the results of factor analysis indicate that West Seattle appears to have four separate sources; sea salt, ammonium nitrate, arsenic + lead, and acid sulfate.

Comparison of Seattle and Bellingham Rainwater

To help assess the degree that Seattle area emissions impact Northern Puget Sound, Bellingham data has been compared to Seattle rainwater data. Figures 14 - 16 compare West Seattle and Bellingham precipitation concentrations for 5 species. These results indicate much lower concentrations of SO_4 and arsenic in Bellingham when compared to Seattle and Tolt indicating that if Seattle and Tacoma area sulfur and arsenic emissions are transported this far North that they are considerably diluted. For most other ions, the concentrations at Bellingham are similar to those measured at the other sites. The Bellingham site is downwind during rain of most, but not all of the Anacortes - Bellingham area sources of SO_2 and NO_x. Our Bellingham rainwater composition is similar to the composition of rain just north of the U.S. - Canadian border (McLaren, 1982).



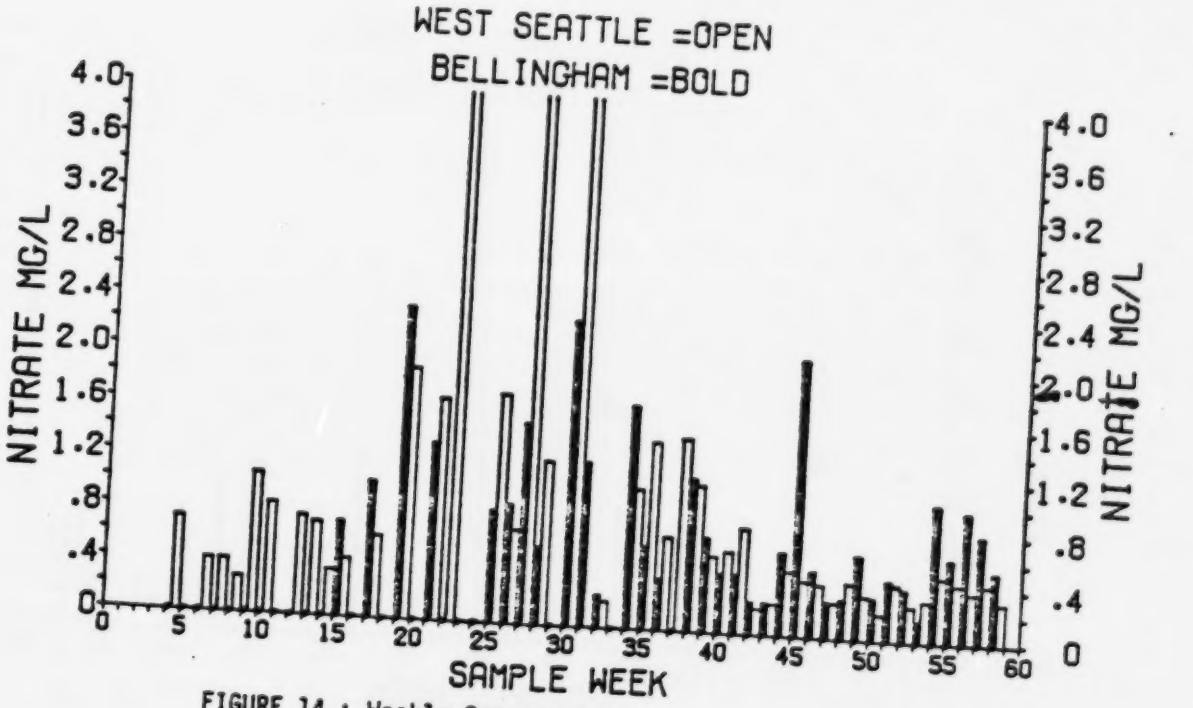
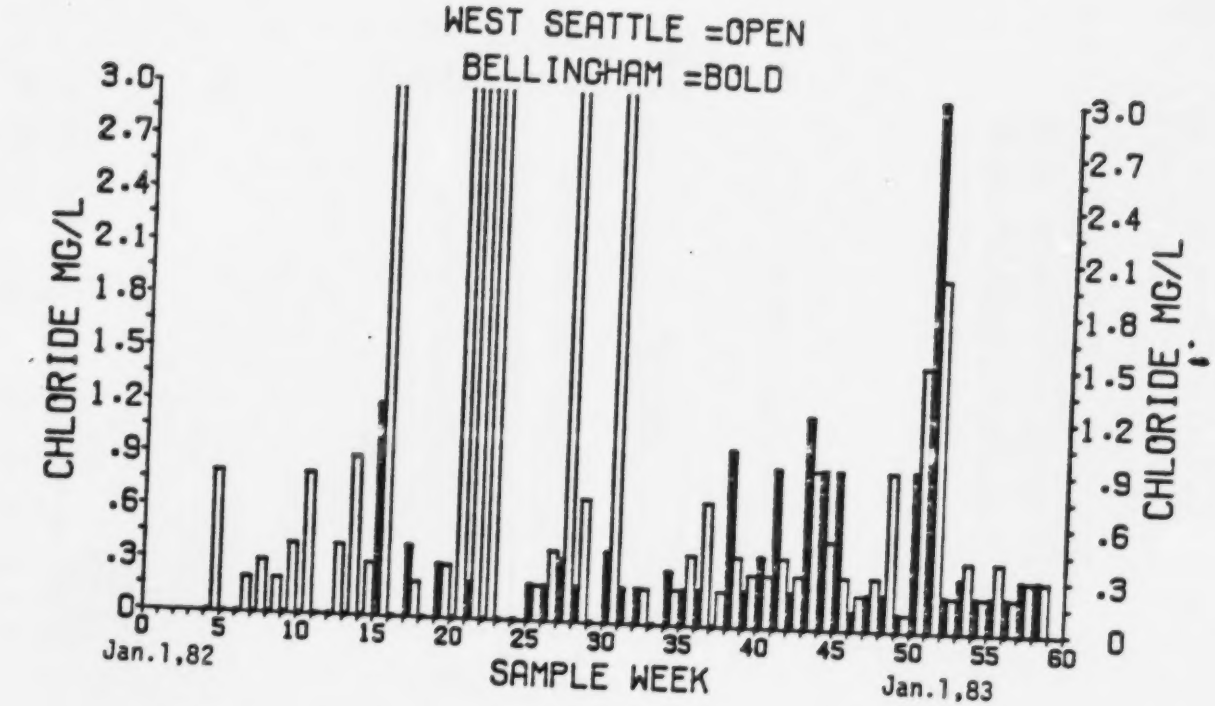


FIGURE 14 : Weekly Concentration



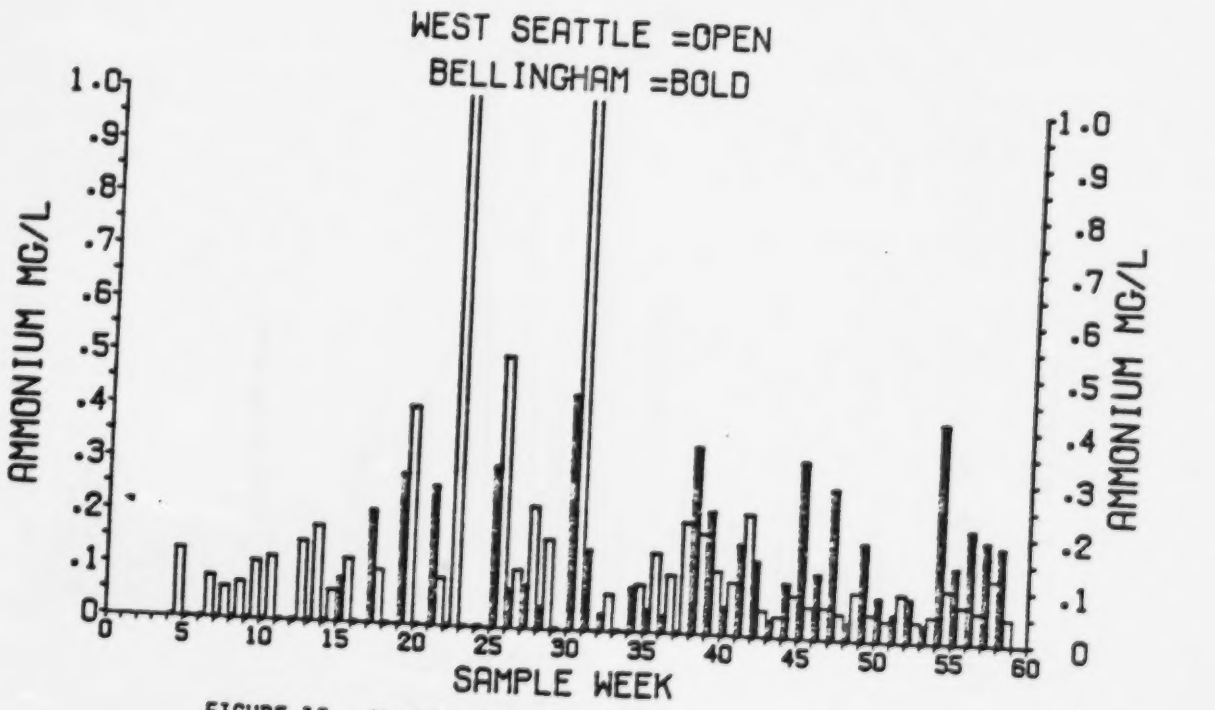


FIGURE 15 : Weekly Concentration

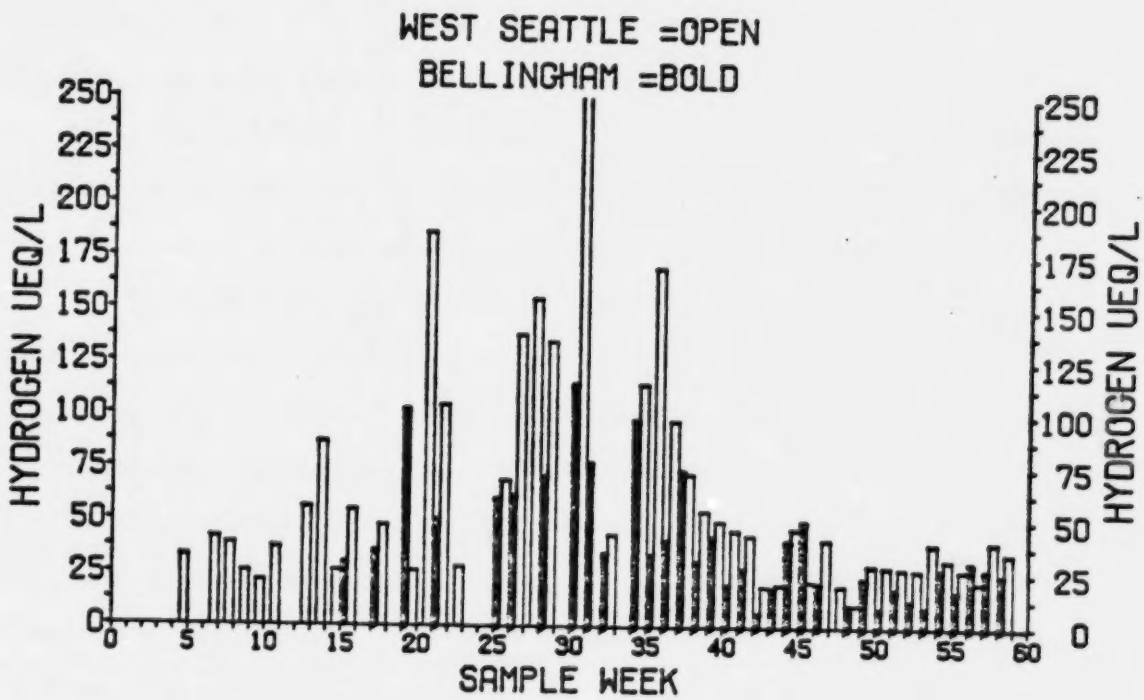


Figure 16: Weekly Concentration

VI Seasonal Variability

The data collected in this study have been analyzed to determine whether rainfall acidity and composition vary with the time of year. This information is of interest for several reasons: 1) Variability in emissions, transport, atmospheric chemistry or rainfall can alter deposition. 2) Sensitivity of biological systems may depend on time of year. Relationships between impacts and sources may require understanding of seasonal variability of the parameters listed above.

Figures 17 and 18 display the weekly sample volume at each of the four sites. The minimum in rainfall in the summer is accompanied by higher concentrations of most species. A summer season has been arbitrarily designated from April 27 until September 7, 1982 with the remainder of the year referred to as winter. Weekly volume weighted average sample concentrations for each season are listed in Table 5 for four species of interest: pH, nitrate, sulfate and calcium. The ratio of the concentrations from the average summer sample to the average winter sample has been calculated for each site. Seasonal variation in emissions and atmospheric chemistry couple with variation in precipitation amount to modulate deposition. In the mid-western US, for example, the sulfate levels are highest in summer as is precipitation amount. This produces a strong maximum in acid deposition. By comparison, in western Washington, the increase in concentration in Summer is balanced by a decrease in precipitation to produce a relatively constant level of deposition.

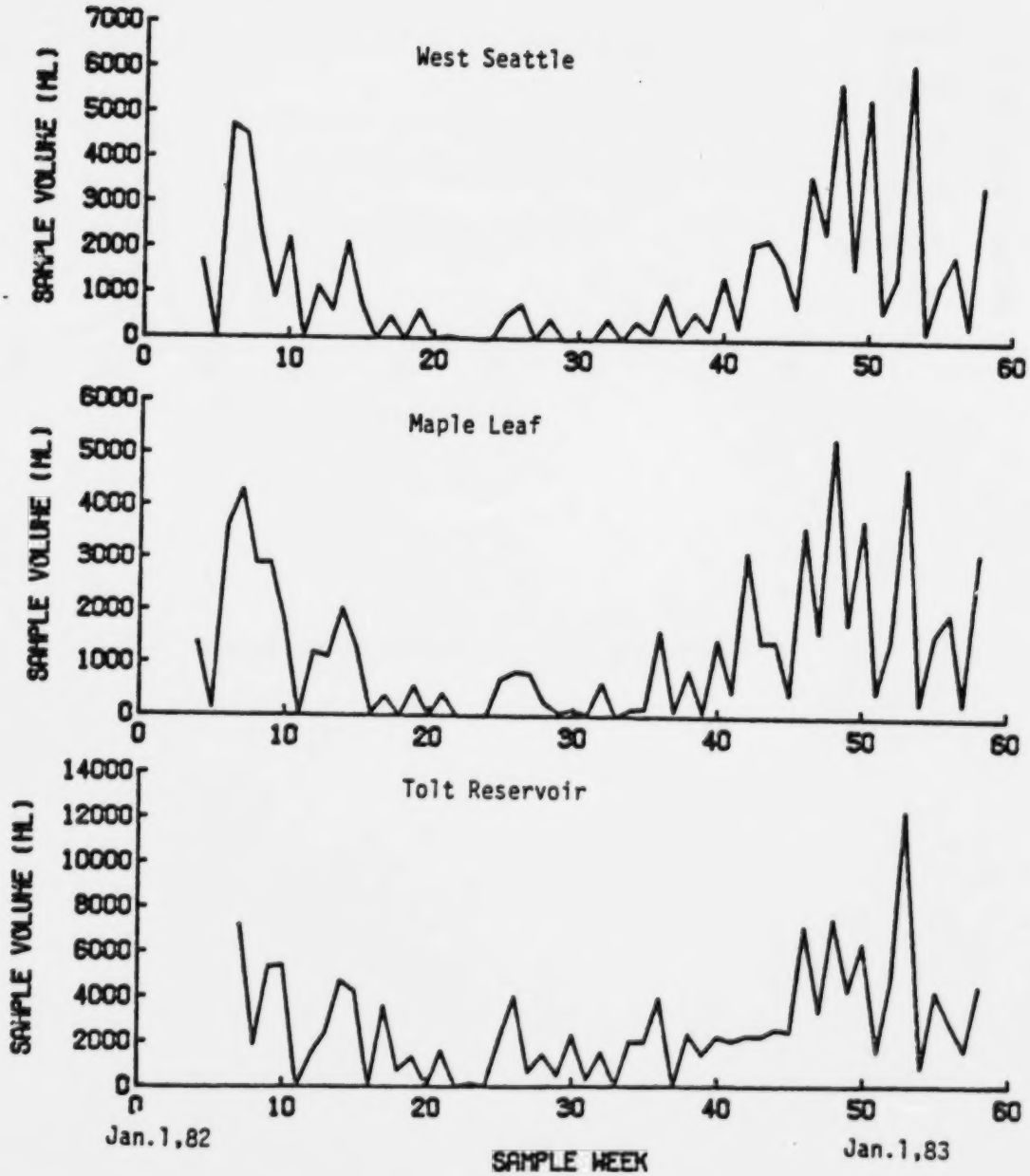
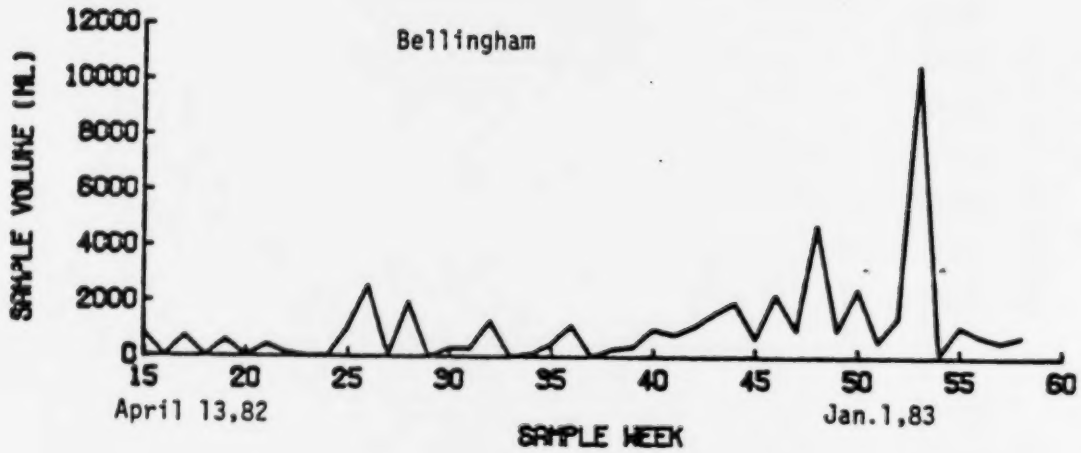


FIGURE 17 : Weekly Rainwater Sample Volume



FIGUPE 18 : Weekly Rainwater Sample Volume

Table 5 shows that in 1982-83 there was a marked seasonality to volume weighted concentration. We find that calcium, nitrate, sulfate and hydrogen ion are 2 to 5 times more concentrated in summer than in winter in Western Washington rainwater. Rainfall quantity decreased in the summer: In the summer, Seattle sites received 12 to 16 percent of average weekly winter rainfall, while the Tolt River and Bellingham received about 33 percent of their weekly winter rainfall. Figures 17 and 18 show sample volume versus time for each site.

The combined effect of higher concentration and low rainfall rates in the summer produces different seasonal deposition patterns at the four sites monitored in this study. Both Seattle sites received higher mean weekly wet deposition of sulfate, nitrate, ammonium, and hydrogen ion in the winter. The Tolt Reservoir received higher average weekly wet deposition of all four species in the summer than in the winter. For three species: sulfate, nitrate and NH_4, Bellingham received higher weekly wet deposition in the winter. For hydrogen ion, Tolt Reservior and Bellingham received higher weekly hydrogen ion deposition in the summer. Table 6 presents ratios for the rainwater concentrations, volume, and wet deposition for the average weekly sample at each of the four sites.

TABLE 5

Summer/Winter Variability in Precipitation Composition
Effects on Concentration (Weekly Volume Weighted Mean)

Site		W Seattle	Maple Leaf	Tolt R.	Bellingham*
Analyte					
pH, field	summer	4.06	4.05	4.15	4.21
pH, field	winter	4.48	4.47	4.79	4.75
SO_4 (excess) (mg/l)	summer	2.77	2.64	1.76	1.33
SO_4 (excess) (mg/l)	winter	1.24	1.15	0.55	0.70
NO_3 as N (mg/l)	summer	0.26	0.29	0.27	0.20
NO_3 as N (mg/l)	winter	0.09	0.11	0.07	0.09
Ca (total) (mg/l)	summer	0.32	0.18	0.08	0.08
Ca (total) (mg/l)	winter	0.12	0.09	0.04	0.04
Volume(ml)	summer	209	273	1272	516
Volume(ml)	winter	1804	1790	3475	1486

Summer Season = April 27 to September 7, 1982 (19 weeks)

Winter Season = February 16, - April 26, 1982 and September 8, 1982 - February 15, 1983 (33 weeks)

*Winter Season for Bellingham = 24 weeks

TABLE 6

Summer/Winter Variability of Rainwater

Ratio of Weekly Average Concentrations
(summer/winter)

Site Species	W Seattle	Maple Leaf	Tolt R	Bellingham
SO_4 (excess)	2.2	2.3	3.2	1.9
NO_3	2.9	2.6	3.9	2.2
Ca	2.7	2.0	2.0	2.0
H+	2.7	2.6	4.4	3.4

Volume Ratio = (winter/summer)

	W Seattle	Maple Leaf	Tolt R	Bellingham
Sample Volume	8.6	6.6	2.7	2.9

Deposition Ratio = (winter/summer)

	W Seattle	Maple Leaf	Tolt R	Bellingham
SO_4	3.9	2.9	.86	1.5
NO_3	3.0	2.4	.68	1.3
H+	3.2	2.6	.63	.84
NH_4	2.9	2.3	.65	2.0

VI Relation of Emissions to Rainwater Composition

Previous modeling of industrial influences on rain quality have focused on sulfur emissions and subsequent wet deposition because sulfate appears to dominate acid deposition in most areas. We had hoped to use trace metals emitted by specific souces to estimate contributions of ASARCO, other industries and urban population centers to sulfate and nitrate deposition in western Washington. This was not possible because of the low levels of these trace metals. An alternate method has been used to estimate the sulfate contributions by different sources in western Washington. We have chosen to model sulfate concentrations because sulfate contributes 65 to 75 percent of the acidity in Western Washington rainwater from charge balance and correlation of sulfate and hydrogen ion concentrations. Sulfate deposition is calculated by dispersing emissions during rain into a 16 segment wind rose and assuming a conversion rate for SO_2 to SO_4 and a washout rate. An approximation of other SO_2 contributions to sulfate in Western Washington rain has been made by assuming two emission points located in Tacoma and Seattle and applying the model used by Vong (1982). It should be recognized that the calculation of diverse SO_2 sources as single point sources in Seattle and Tacoma is only intended to roughly approximate their contributions to local rain chemistry. The calculated sulfate deposition from the major point sources in Tacoma (copper smelter) and Centralia (power plant) are most suitable for estimating long term averages, one year or longer. The model predictions in Table 7 indicate that, for average wind and rain patterns, the Tacoma copper smelter is the largest source of sulfate in Puget Sound

rainwater, contributing about 60 percent in West Seattle, 45 percent at Maple Leaf reservoir, and approximately 35 percent at the Tolt reservoir in the Cascade foothills. The Tolt calculation is uncertain since only 84 percent of measured sulfate is predicted. This apportionment of Puget Sound rainwater sulfate appears to account for 84 to 96 percent of the measured concentrations for 1982-83 as shown in Table 7. Figure 19 presents the results of calculations for sulfate deposition from emissions of the ASARCO Copper Smelter in Tacoma into 16 sectors of 100 km length from the emission point.

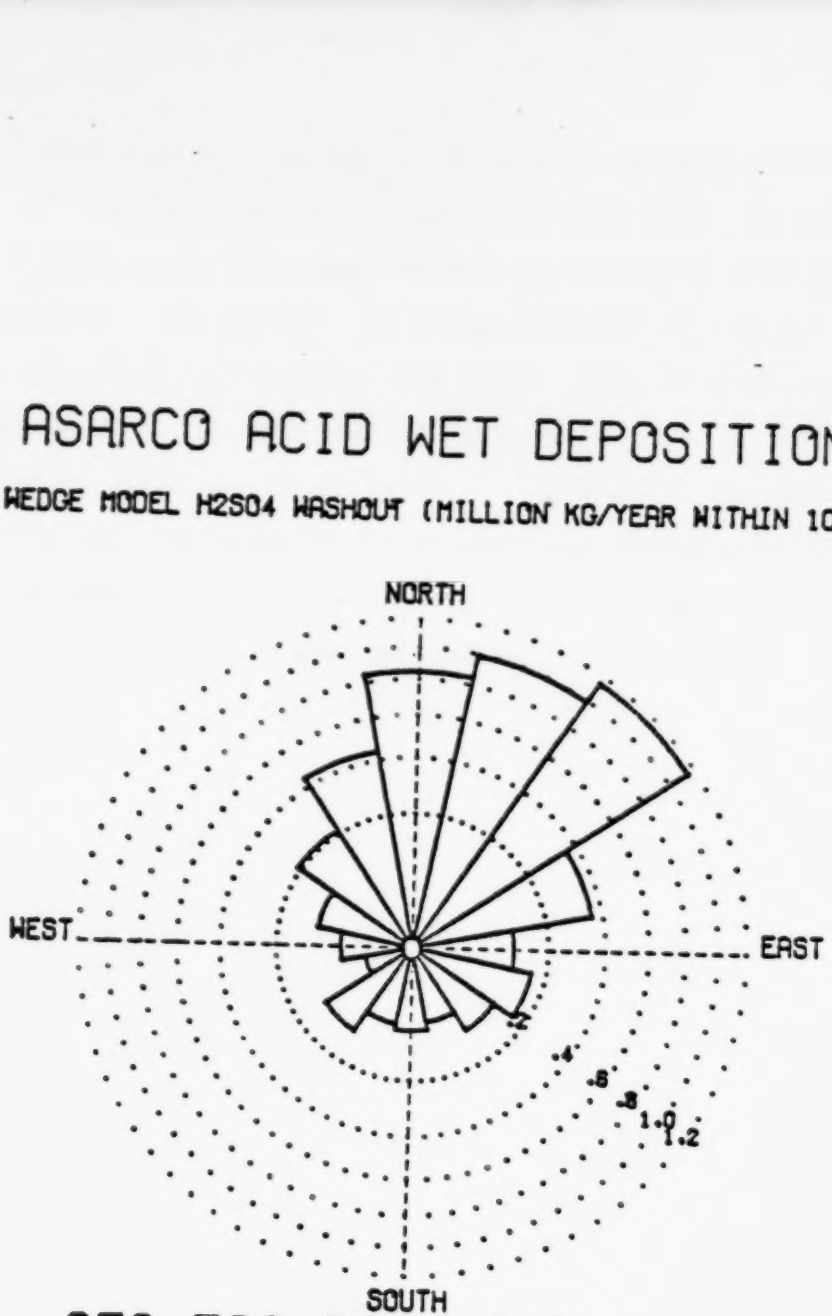


FIGURE 19 : Calculated Sulfate Wet Deposition for the Tacoma Copper Smelter (Vong,1982)

TABLE 7
Summary of Calculations of Contributions To SO_4
from Sources of Sulfate in Rainwater

	W Seattle (mg/l)	Maple Leaf (mg/l)	Tolt R (mg/l)
1. Measured:	Rainwater Concentration:		
Background (excess)	0.22(16%)	0.22(17%)	0.22(27%)
Sea Salt	.08(6%)	.06(5%)	.06(7%)
2. Modeled*			
Tacoma Smelter	0.88(62%)	0.60(45%)	0.28(34%)
Centralia power pl	.09(6%)	0.08(6%)	.07(9%)
Pierce County SO_2	.09(6%)	.06(5%)	.03(4%)
King Co SO_2	Negl.	.23(17%)	.03(4%)
3. Total Predicted	1.36(96%)	1.25(94%)	0.69(84%)
4. Measured(1982-3) (mg/l)	1.42	1.33	0.82
Underprediction (mg/l)	0.06(4%)	0.08(6%)	0.13(16%)

*Reference: Hutcheson and Hall, 1974; Vong, 1982

Assumptions:

1. Emission rates: Pierce County SO_2 = 1500 kg/HR
   King County SO_2 = 2670 kg/HR
   Smelter SO_2 = 14273 kg/HR
   Centralia Power plant SO_2 = 6213 kg/HR
   (Vong, 1982; PSAPCA, 1983)

2. Meteorology and Scavenging efficiency: Winds are average climatological values and Scavaging as reported by Vong (1982).

3. Area SO_2 Sources: Pierce County SO_2 and King County SO_2 are modeled as point sources located in downtown Tacoma and the Duwamish Valley, respectively.

NADP data for the Hoh River indicate much lower concentrations for sulfate, nitrate and hydrogen ion near the coast of Washington than in the Puget Sound area. Sections III and V utilize Hoh River data as background to be subtracted from Seattle precipitation concentrations in this study. Our data is compared to other measurements in table 8.

Table 8
Rain Chemistry Data Measured by Other Investigators
Comparison of Western Washington Rainwater Excess Concentrations with Other Geographical Areas (Micro Equivalents / Liter)

Analyte	Western Wash. 1982-83	Sjoangen Sweden Sweden 73-75	Hubbard Brook NH 1963-74	Poker Flat AK 79-81
NO_3	7.1 - 8.6	31	23.1	1.9
Cl	11.3 -16.3	18	14.4	2.6
SO_4	16.7 -29.2	69	59.7	7.2
NH_4	3.6 - 5.7	31	12.1	1.1
Na	9.6 -11.3	15	5.4	1.0
K	0.7 - 0.9#	3	1.9	0.6
Mg	2.5 - 3.4	7	3.7	0.2
Ca	2.2 - 6.4	13	8.6	0.1
H+	25 - 39	52	73.9	11
pH	4.4 - 4.6	4.3	4.13	4.96
SO_4 Dep. (meq/m^2year)	26 - 35	70	80	2.1
H+ Dep. (meq/m^2year)	36 - 56	53	82 - 113	3.1

Reference: This study; Granat, 1978; Likens,1976; Galloway,1982)

#Concentration value of questionable accuracy.

Explanations for increased under-estimation of SO_4 deposition with distance include:

1) Inability of model to predict increased nucleation scavenging of SO_2 for large oxidation and transport times and distances.

2) Errors from modeling Seattle SO_2 source emissions as one point source.

VI Measurements by Other Investigators

The results of this study indicate that rainwater in Western Washington is acidic with measureable concentrations of heavy metals and sea salt. Comparison of our data with other studies of rainwater chemistry indicate that the areas known to experience damage from acid deposition such as southern Sweden and New England receive 2 to 3 times more sulfate and 1.5 to 2 times more hydrogen ion than Western Washington (Likens, 1976; Granat, 1978). Data collected in Vancouver, B.C. indicate higher nitrate and calcium concentrations and lower hydrogen ion concentrations than in Seattle rainfall (Barrie, 1983). However, Seattle receives three times the hydrogen ion and 3-4 times the sulfate concentrations that were detected at a remote site with low rainfall rates located in Poker Flat, Alaska (Galloway, 1982).

Table 8 , Continued
Comparison of Western Washington Rainwater Excess Concentrations with Nortwest Rain Data (Micro Equivalents / Liter)

Analyte	Port Hardy BC 1977-79	Vancouver BC 1980	Hoh River WA 1980-82
NO_3	5.9	13.5	1.5
Cl	81.4	26.4	38.3
SO_4	28	36	8.5
NH_4	6.4	10.9	0.3
Na	76.8	23.2	31.4
K#	3.0	3.4	0.8
Mg	17.4	6.2	7.4
Ca	11.2	27.4	3.1
H+	11.5	17.5	4.06
pH	4.94	4.76	5.39

#Concentration value of questionable accuracy.

	Deposition, gm/m^2 per Year		
Sulfate (Total)	2.23	2.45	1.37
H+	0.019	0.025	0.014
Reference:	(Barrie, 1982)	(Barrie, 1982)	(Yanish, 1983)

A recent compilation of rain chemistry data indicates that Western Washington rainfall has lower concentrations of hydrogen ion, nitrate, lead, zinc, and sulfate than the heavily polluted Ohio Valley and Northeastern U.S., but Western Washington receives higher concentrations of hydrogen ion and sulfate than most of the northwestern U.S. (Munger, 1982).

Comparison of our data with other investigations of western Washington rainfall, shown in Table 8, found general agreement. One event study in Seattle showed arsenic and sulfate values similar to our data but observed higher zinc, cadmium, potassium and calcium concentrations (Larson et al., 1975). Dethier (1981) found higher copper, lead, and zinc but less arsenic in the North Cascades than at the Tolt River site in this study. A six month study near Snoqualmie Pass found consistently higher calcium and nitrate concentrations than detected at the Tolt in this study (Logan et al., 1981). Logan's samplers were located near automobile traffic on I-90 and may have found a locally higher nitrate concentration for this reason. Measurements of precipitation ionic concentrations from month duration, wet only samples on the roof of a nearby University of Washington building found lower pH (4.2) and higher concentration values for all species than we report (USDOE, 1979; 1981). Their data may not be representative of the Seattle area due to local sources of nitrate, calcium and sulfate found in our precipitation samples from the University of Washington. Our study found lower calcium than other studies reviewed here. This could be due to low dry deposition by use of the wet/dry rain sampler in this project and locating the samplers in grassed areas.

VIII. Conclusions and Recommendations

1) Deposition of acid in the Washington Cascades is at or above the reported threshold for acidification of sensitive lakes with low capacity to neutralize acid inputs. Sensitive lakes are common in the Cascade Mountain Range.

2) Acid concentrations and acid wet deposition in western Washington are less than one-half that received in heavily impacted areas in the northeastern US and Southern Sweden but higher than most of the northwestern U.S. The average pH in western Washington was 4.4 - 4.6, about 0.25 pH units less acid (higher) than in northeastern US and southern Sweden. Western Washington rain acidity is at the level reported to be on the threshold of damage to aquatic populations.

3) Rainwater in north Seattle and at the Tolt Reservoir show similar compositions, probably due to similar sources impacting both areas.

4) At the Seattle sites, acid deposition was higher in winter than in summer. Deposition was higher in summer than in winter at Tolt and Bellingham. This difference reflects the higher precipitation in summer at Tolt and Bellingham compared to the other sites.

5) Western Washington rainfall is acidic with seasonally higher concentrations of most ionic species in the summer.

6) Models suggest that the dominant acid sources for Seattle and Tolt rainfall appear to be the Tacoma Copper Smelter for sulfate and transportation emissions for nitrate. This is largely based on the contributions of ASARCO and transportation to SO_x and NO_x emissions in Puget Sound.

7) Rain in Bellingham has lower concentrations of sulfate and was less acid than that at Seattle sites.

8) Rain from oceanic air at Hoh River sampling site contains about 16 percent of the sulfate concentration and 17 percent of the nitrate in Seattle rainwater.

9) The deposition and concentrations of major ions were not appreciably degraded by sampling and analysis procedures except for trace metal species, potassium and phosphate. The precision and sensitivity of analytic methods was not sufficient to accurately determine trace metal concentrations in western Washington rainwater.

B. Suggestions for Future Work

1) Analysis of the trends in acidic precipitation in western Washington will require long term monitoring of rainwater composition in western Washington. A major problem in our understanding of acid precipitation in eastern US and Canada is lack of long term deposition data. This suggests that the current program sampling rain in western Washington should be continued in the long term.

2) Collection of event length precipitation samples with more extensive transport wind-field measurements would help to identify source-receptor relationships in western Washington rain quality. Electric Power Research Institute (EPRI) plans such a program for 1983 - 1984.

3) Improvements are needed in sensitivity of analysis for trace metals. These measurements are useful to trace acid deposition to specific sources or types of sources in Western Washington. Trace metal analysis of Hoh River rainwater would be useful to to discover man's impact at this coastal site.

4) The existing data set indicates there may now be damage to fish resources in Cascade lakes. To clarify this problem, measurements of lake buffering capacity, biology and acid input are needed.

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Appendix A: Accuracy of Data

The data that result from this program must be sufficiently accurate to satisify the anticipated applications for the data: to characterize the precipitation in terms of acid inputs to the land and to trace the acidifying species to sources or classes of sources. The data will fulfill these needs if the samples are collected and transported to the analytic laboratory without contamination and the analysis is done with sufficient accuracy and sensitivity to quantify the dissolved species in the rain.

Samples of precipitation were collected in automatic rain sensing wet-dry collectors using acid washed plastic buckets. The sample duration was one week and samples were collected over the period January 15, 1982 - February 15, 1983. Volume, temperature and conductivity were measured at the time of collection; field pH and conductivity were measured after about 24 hours storage at room temperature at the University of Washington. All sample handling and storage used Nalgene plastic bottles and labware. The last rinse of each bucket was analysed to detect contamination of the bucket. Samples were sent to the EPA laboratory at Manchester for analysis and storage at 4° C.

The analytic method and detection limits reported by the EPA laboratory are listed in Table 9. Precision and accuracy of the analytic methods were checked periodically with EPA Quality Control and Performance samples.

TABLE 9

Analytic Method and Detection Limits, EPA Manchester

Analyte	Method	Limit of Det., ug/l*
SO_4	Auto Analyser - Colorimetric	500
NO_3 as N	"	2
NH_4 as N	"	2
Cl	"	2
PO_4	"	2
		Analytic Instrument PE5000/PE360
Na	Flame Atomic Absorption (AA)**	5 / 20
Mg	"	10 / 10
K	"	1 / 10
Ca	"	1 / 30
		PE5000-Zeeman/PE403-HGA2100
As	Graphite Furnace (AA)**	0.1 / 2
Cu	"	0.1 / .8
Pb	"	0.1 / 1
Zn	"	1 / 10
Cd	"	0.1 / 0.1

*Anal. Chem. 52, 2247 (1980)

**Two different AA instruments were used during this program. The new analytic instrument that increased sensitivity was used after October of 1982.

Analytic accuracy was tested by comparing analytic results against solutions prepared in our laboratory for concentrations and conductivity and NBS potassium phthalate pH reference for pH. The results of these comparisons of analysis to our test solutions is given in Table 10 and for rainwater in 11.

TABLE 10
Comparison of Analytic Results to Standards
Analytic Result = (Slope) X (Standard) + Intercept

Analyte	Method	Slope	Intercept	R^2
SO_4	Auto. Colorimetric	1.03	.114	.99
SO_4	Ion Chromatograph*	0.99	.065	.99
Cl	Auto. Colorimetric	0.78	0.83	.99
NO_3	Ion Chromatograph*	1.05	-0.015	.99
NO_3	Auto. Colorimetric	0.97	0.063	.99
Conductivity	Pt Electrode	1.08	0.98	.99

Comparison of UofW and EPA pH Against Standards

pH	Glass Electrode	pH(UofW) = pH(EPA) - 0.06

*Hegg, D. A.; Atmos. Sciences, Univ. of Wash.

TABLE 11
Comparison of Sulfate and Nitrate Analysis Techniques for Rainwater Samples By Least Squares Regression

*Hegg(ion chromatograph)=(Slope)X(EPA(colorimetric))+Intercept

	Slope	Intercept	R^2
Sulfate	1.15	-.054	.72
Nitrate	.93	.010	.98

*Hegg, D. A.; Atmos. Sciences, Univ. of Wash.

We also tested precision by submitting split samples, two duplicate samples from one precipitation collection identified to the laboratory as different samples. The results of this test is presented in table 12.

Table 12

Estimates of Analytic Uncertainty
by Split Samples of Rainwater
Least Squares Regression of Replicate Analysis,
(Sample 2) = (Sample 1) X (Slope) + (Intercept); mg/l

Analyte	Slope	Intercept	R^2
SO_4	1.06	-.029	.95
Cl	1.03	-.025	.98
NO_3 as N	1.00	-.001	.99
NH_4 as N	1.02	-.001	.97
Na	1.05	-.015	.99
Ca	.86	.006	.56
K	.22	.012	.03
Mg	1.04	-.001	.98
Cu	1.53	.08	.45
As	.65	.40	.45
Pb	.87	.60	.39
Zn	.42	.56	.28
Cd	-.44	.55	.01
Conduct.	1.02	-.13	.99

Each analyte: 19 pairs of differently labeled identical samples

Considering the requirements of this program, we find the accuracy of chemical analysis acceptable for the major species (except calcium) based on tests of accuracy and precision. Ratios of reported concentrations indicate 8-13 percent variability in the results for sulfate in the 0.6 to 2.0 mg/l range which includes most Puget Sound rainwater concentrations and 8 percent for nitrate. Therefore, the choice of techniques by EPA for these two critical anions appears to give good results for the concentrations typical of Puget Sound rain. Except calcium, potassium and the five trace metals, all species have average differences of reported concentrations for split samples of less than 20 per-cent of the average value.

The sensitivity of the analytic techniques used for the trace metals and potassium was not sufficient to use the results to trace acid deposition to specific sources or classes of sources in this program. Analysis of the five trace metals species (lead, arsenic, copper, zinc, and cadmium) was performed on unfiltered, unacidified aliquots of rainwater. All trace metal species, except lead, show poor reproducability of measured concentration at the levels that exist in western Washington rain. Zinc and cadmium also show poor correlation of the data with the least squares regression line.

Explanations for the relatively poor analytic precision for metals include:

1) Analytical insensitivity at the low concentrations found in Washington rainwater,

2) Possible loss of metals to the walls of the sample bottle for these species because sample was not acidified prior to storage for later AA analysis.

Detection limit problems are real for rainwater and explanation 1) probably is important to the calculated precision. However, explanation 2) may be important. NADP specifies acidification to pH = 2 for these analyses (Peden et al., 1979) and this should be done in future studies.

Due to analytical uncertainties, zinc and cadmium have been omitted from the analysis in this report except for inclusion in mean annual average volume weighted concentrations. Data for potassium, lead, arsenic, and copper were included in factor analysis although caution is suggested in drawing conclusions from these data.

Hydrogen ion was measured with a glass pH electrode at the University of Wash. (field) and at the EPA analytical labatory (lab). Comparison of field (University of Wash.) pH measurement of NBS and potassium phthalate pH reference standards found a mean negative bias of 0.07 pH units by University of Wash. Comparison of lab (EPA) and field (University of Wash.) was made for rainwater H+ concentration calculated from measured pH, shown in table 10, indicates that field pH averages 0.06 to 0.10 pH units less than lab pH.

Laboratory pH was not taken for some summertime samples due to low sample volume. Charge balances were calculated for these low volume samples using pH from regression of field pH with lab pH to generate the missing lab pH values.

TABLE 13

Relationship Between Field and Lab Rainwater Hydrogen Ion Concentration, Calculated from pH
H+(Lab) = H+(Field) X (Slope) + Intercept
Least Squares Regression, Units = H+(ueq/l)

Site	Slope	Intercept	R^2	# Observs.
Maple Leaf	.80	.96	.74	37
West Seattle	.91	.47	.80	36
Tolt River	.94	.39	.94	45
Bellingham	.84	.85	.87	31

Four explanations for lower field pH values than lab pH are considered:

1) Negative bias in field pH measurement techniques is suggested by audit samples.

2) Leaching of small amounts of insoluble particulate material in rainwater into solution during transport and storage (Peden, 1978).

3) Consumption of organic acids by algae during sample storage (Galloway, 1982).

4) Absorption-desorption reactions including weak acids, from SO_2 or bases from laboratory air ammonia.

Bias about equal to the difference between UofW field and EPA lab pH of rainwater samples was detected using standards. Organic acids and effects of laboratory atmospheric gases are expected to be fairly small in comparison to the strong acid content and probably are not the cause of lower field pH. The second explanation seems most plausable. Some insoluble cations are present as indicated by comparison of filtered and unfiltered aliquots. A ring appeared in sample buckets after collection on several weeks also indicating the presence of small amounts of insoluble material in Western Washington rainwater. Rainwater can contain basic, insoluble (often soil derived) minerals due to below cloud scavenging of dust by falling rain.

We examined the effect of ambient temperature storage in terms of change in sample pH during the one day to one week residence of the sample in the bucket prior to analysis. pH measurements of rainwater stored at 20° C found a small pH increase of within two weeks after collection and little change between 2 and 8 weeks. These observations are consistent with a previous study indicating replacement of hydrogen ion by particulate calcium in room temperature storage of unfiltered solutions. The samples collected in this study were not refrigerated for 1 - 7 days in the field and during a 2 or 3 day period between collection and arrival at EPA lab. pH and conductivity were measured at the EPA laboratory within 24 hours after sample delivery. The samples were then filtered and analysis performed for sulfate, nitrate, ammonium, chloride and phosphate. Unfiltered samples were reserved for determination of sodium, potassium, calcium, magnesium and

other metals. Samples were maintained at room temperature until pH and conductivity were measured, the refrigerated at 4° C until analysis.

The effect of insoluble materials on sample composition was evaluated by comparison of 27 filtered versus unfiltered aliquots of the four cations of primary concern the charge balance. The results indicate that unfiltered aliquot concentrations range from 1-27 percent higher than concentrations in filtered aliquots. Table 14 presents a regression analysis for filtered versus unfiltered cations.

TABLE 14
Comparison of Filtered vs Total Concentrations
For Important Cations

Least Squares Regression
Filtered = (slope) X (Total) + (Intercept), mg/l

Species	Slope	Intercept	R^2
Na	.893	.022	.61
Ca	.737	.006	.45
K	1.04	-.003	.97
Mg	.912	.002	.90

Note: 27 samples of rainwater were measured for each analyte.

The data in Table 14 is used in correcting charge balance for particles as described on the following page and in table 15.

A common test of the accuracy of the analytical methods and completeness of the choice of analytes is the balance of positive and negative ions. A ratio of 1.0 confirms electro-neutrality and implies that the analysis scheme is appropriate. Table 15 presents the mean and standard deviations (by site) of this charge balance ratio. Measured cations exceed anions by about 18 percent. Possible explanations for this cation excess include;

1) Analytical error, considered unlikely as discussed earlier.
2) Presence of low solubility particles detected by AA and not the Technicon Auto-Analyzer is considered to be the likely source of this charge inbalance.

Regression analysis of filtered versus unfiltered cations was used in the charge balance equation to predict the charge balance ratio in filtered aliquots as shown in the right column of Table 15, below. The results of this analysis indicate that most of the charge balance error is due to insoluble cations.

Table 15
Charge Balance of Rainwater Samples

Site	Measured (+)/(-)	Predicted (+)/(-)
Maple leaf	1.15(.22)	1.00(.23)
West Seattle	1.17(.29)	1.03(.28)
Tolt River	1.21(.40)	1.08(.38)
Bellingham	1.19(.29)	1.00(.29)
All Locations (185 Samples)	1.18(.29)	1.02(.29)
Range of Values (185 Samples)	0.40-3.32	0.33-3.11

Three acidic species which could be present in western Washington rainwater were not measured in this study: bicarbonate, bisulfite, and organic acids (such as formate or acetate anions detected in rainwater by Galloway, 1982). Organic acids can represent up to 25 percent of the acidity of rainwater in very remote locations, especially where agricultural burning is present. Organics are not expected to be important in Western Washington rain except possibly at the Hoh River. Analysis for organic acids was not performed. Carbonic acid in equilibrium with 340 ppm atmospheric CO_2 can be calculated to contribute less than 1.0 ueg/l at pH = 5.0 and less than 0.5 ueq/l at pH = 4.5. Bisulfite and sulfite are more important where high atmospheric SO_2 concentrations occur, as in Tacoma or locations in Seattle near industrial sources. Many difficulties exist in determining HSO_3 in rain:

1) SO_2 in Solution could partly oxidize to SO_4 during the one day to one week that the sample remains in the field or during transport to the EPA Lab.

2) SO_2 may desorb or absorb from the rain sample such that analysis reflects atmospheric levels of SO_2 in the laboratory rather than the sample environmental conditions.

Since acidic solutions shift the partioning of the $SO_2/HSO_3/SO_3$ equilibrium towards gaseous SO_2 (Taylor et al., 1982), the HSO_3 contribution to the charge balance of weekly samples of Western Washington rains is expected to be small away from emission sources.

The Wet-Dry Sampler as a Source of Rain Composition Variability.

The sampler contributes to variability in measured precipitation quality because of uncertainty in the operation of the precipitation detector. If rainwater composition varies during the period of rainfall, the measured composition will be a function of the period during which the sample is collected. The rainwater samplers used in this project detect precipitation using a sensor grid overlying a heated plate. Accumulation of a sufficient volume of rainwater bridges the gap between the plate and sensor, completes an electrical circuit which energizes a motor to move the lid from the wet bucket exposing it to precipitation. The samplers used in this study were of two slightly different designs. The samplers at the Tolt Reservoir and West Seattle required a slightly larger rain volume to actuate the lid than the other locations. To test the combined effect of sampler design and bucket wash consistency on measured rainwater composition, two samplers of different sensor design were co-located at Maple Leaf reservoir during the Summer of 1982. The results of ths comparison are presented in Table 16.

Table 16 presents two types of sources of measurement uncertainty in these rainwater data: analytical and sampling. Co-located sampling variability includes both analytical and sampling variability. With the exception of potassium and trace metals, these results indicate that the combined sampling and analysis related variability ranges from 8 to 29 percent for the species analyzed. These tests show that two analyses display lower relative variability for colocated samplers than for identical split samples for unknown reasons. The potassium analysis is not precise enough to justify any conclusions.

TABLE 16
Variability in Rain Sampling by Fraction Difference for Analysis, Sampling and Site Location by Analyte

Species	Analytical*		Co-located**	
	X	Y	X	Y
SO_4 (mg/l)	.04	(.032)	.20	(.767)
Cl- (mg/l)	.13	(.021)	.12	(.113)
NO_3 as N (mg/l)	.01	(.001)	.12	(.279)
NH_4 as N (mg/l)	.12	(.003)	.28	(.069)
Na (mg/l)	.11	(.013)	.22	(.083)
Ca (mg/l)	.52	(.015)	.23	(.047)
K (mg/l	.87	(.012)	.67	(.081)
Mg (mg/l	.19	(.003)	.29	(.036)
Sample Volume (ml)	---		.13	(18.4)
Conductivity (uS/cm)	.01	(.142)	.08	(1.94)
pH-lab (pH units)		(.03)		(.03)
pH-field (pH units)				(.10)

Where: X = Difference/Average and
Y = Difference in Specified Units
(X and Y are absolute values)

*Analytical Uncertainty determined from split samples.
**Colocated samples collected 5 meters apart at Maple Leaf.

We have compared our precision and accuracy to that of the Canadian program, CANSAP and to the EPRI program, SURE. CANSAP reports uncertanties as about 0.1 pH unit, 20 per-cent on chemical analysis, with variability due only to collection of 5-80 per-cent and variation due to siting for nitrate and 10 to 30 per-cent for sulfate. Calcium and potassium displayed the largest relative variability for their data, similar to this study (Barrie, 1982).

An analysis of EPRI-SURE precipitation chemistry data for colocated samples indicated the following ratios or fractional error in analysis for the following ions in table 17 (Topol, 1982).

Table 17

Fractional Error for Colocated Samples

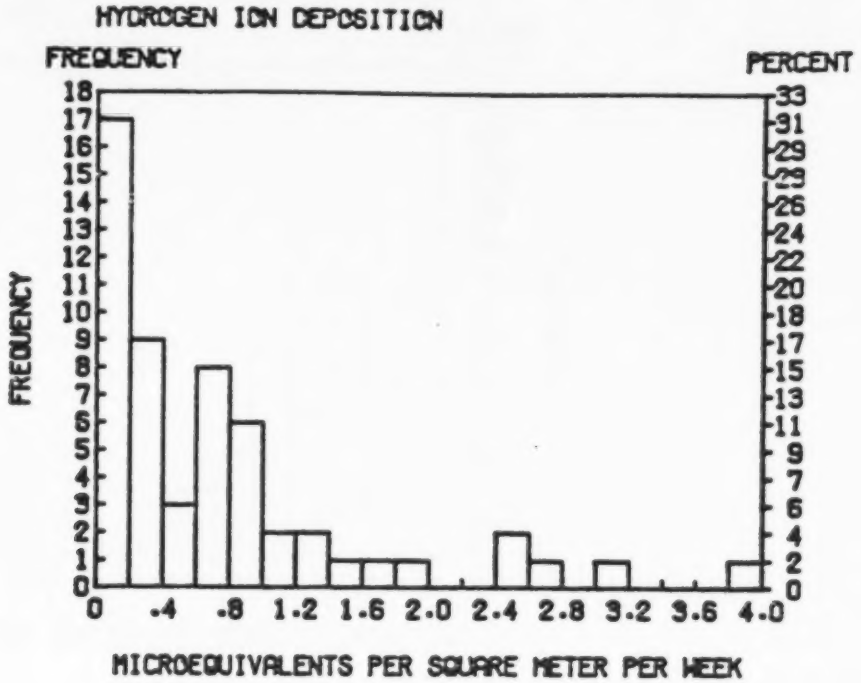
Conduct.	SO_4	NO_3	Cl	NH_4	Na	K	Ca	Mg	Al
.06	.05	.05	.11	.08	.18	.43	.16	.13	.37

pH (error in pH units): 0.06

We conclude that the analyses used in this program suffice to quantify the acid deposition in Western Washington. The analytic precision for trace metals was low enough to reduce confidence in assigning sources to the acid deposition. Increased sensitivity is needed for trace metals and this may be improved by acidifying the samples prior to storage and analysis. Inductively coupled plasma analysis may also improve sensitivity over AA for some trace metals.

APPENDIX B

Frequency of Occurrence of Rainwater Concentrations, Volume, Conductivity, and Deposition Quantity by Sampling Location


HYDROGEN ION DEPOSITION
FREQUENCY
PERCENT
FREQUENCY
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
0 2 4 6 7 9 11 13 15 17 18 20 22 24 26 29 31 33
0 .4 .8 1.2 1.6 2.0 2.4 2.8 3.2 3.6 4.0
MICROEQUIVALENTS PER SQUARE METER PER WEEK

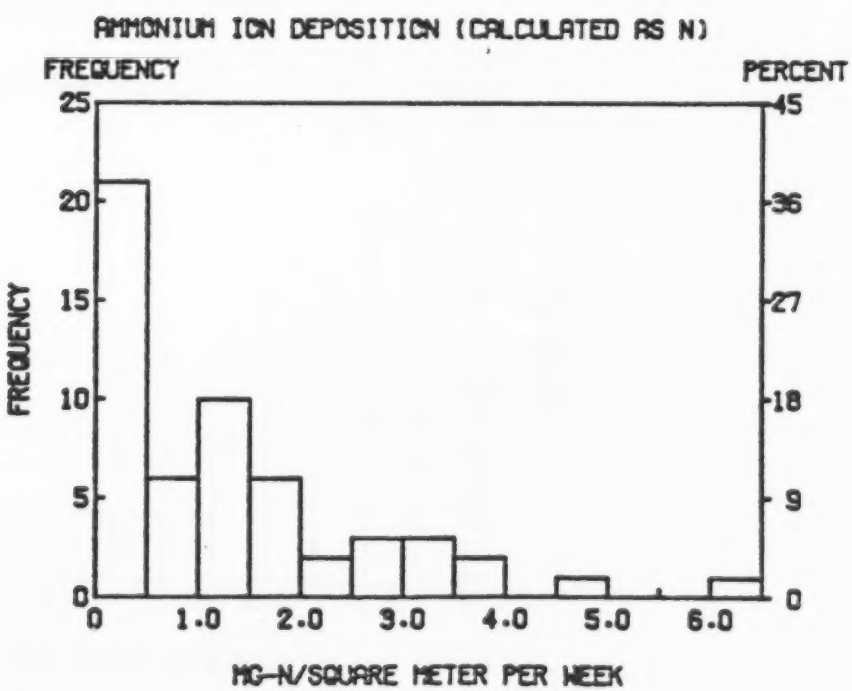
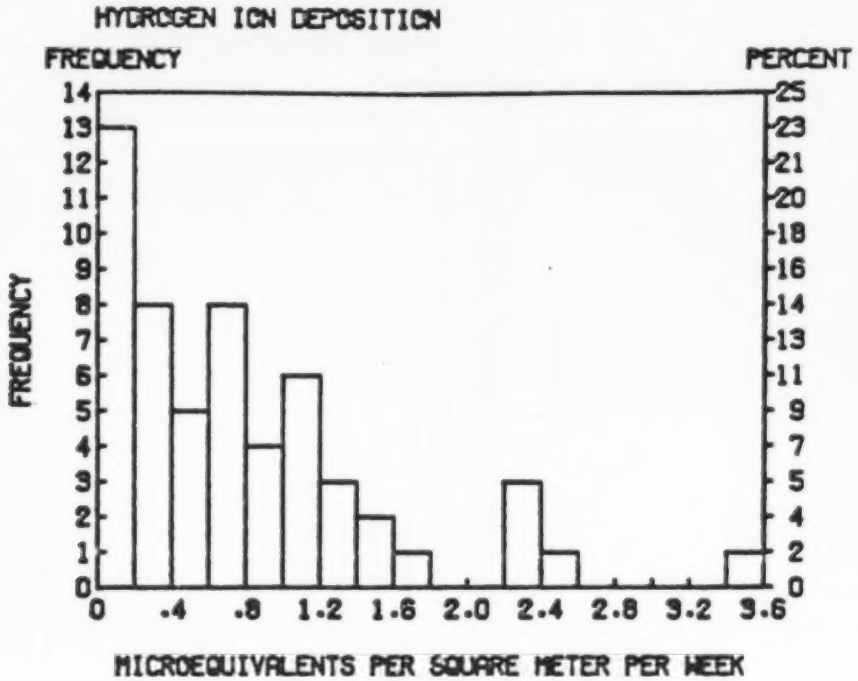

AMMONIUM ION DEPOSITION (CALCULATED AS N)
FREQUENCY
PERCENT
FREQUENCY
0 5 10 15 20 25
0 9 18 27 36 45
0 1.0 2.0 3.0 4.0 5.0 6.0
MG-N/SQUARE METER PER WEEK

FIGURE 20 : Frequency of Occurrence at West Seattle


HYDROGEN ION DEPOSITION
FREQUENCY
PERCENT
FREQUENCY
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
0 2 4 5 7 9 11 13 14 16 18 20 21 23 25
0 .4 .8 1.2 1.6 2.0 2.4 2.8 3.2 3.6
MICROEQUIVALENTS PER SQUARE METER PER WEEK

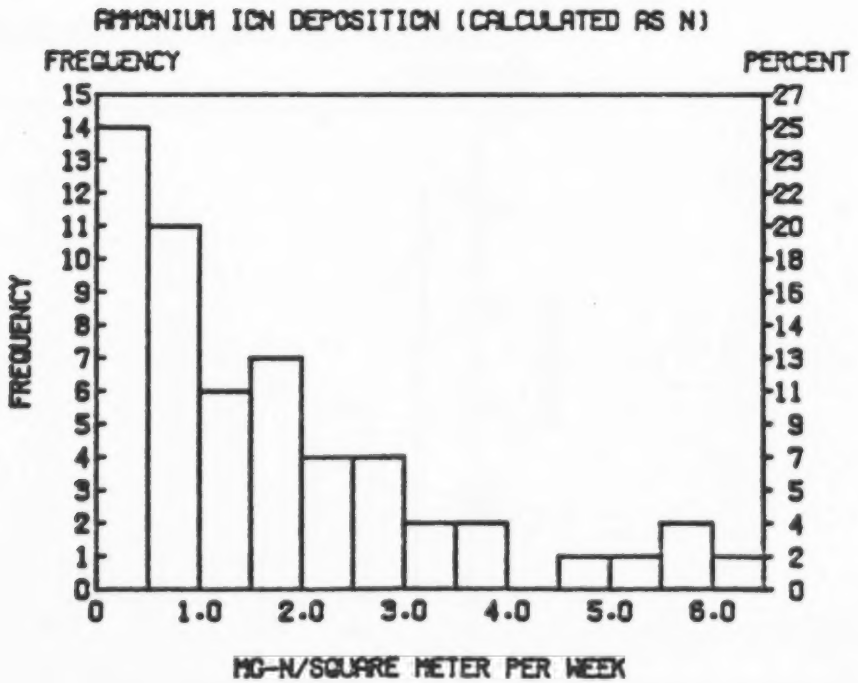
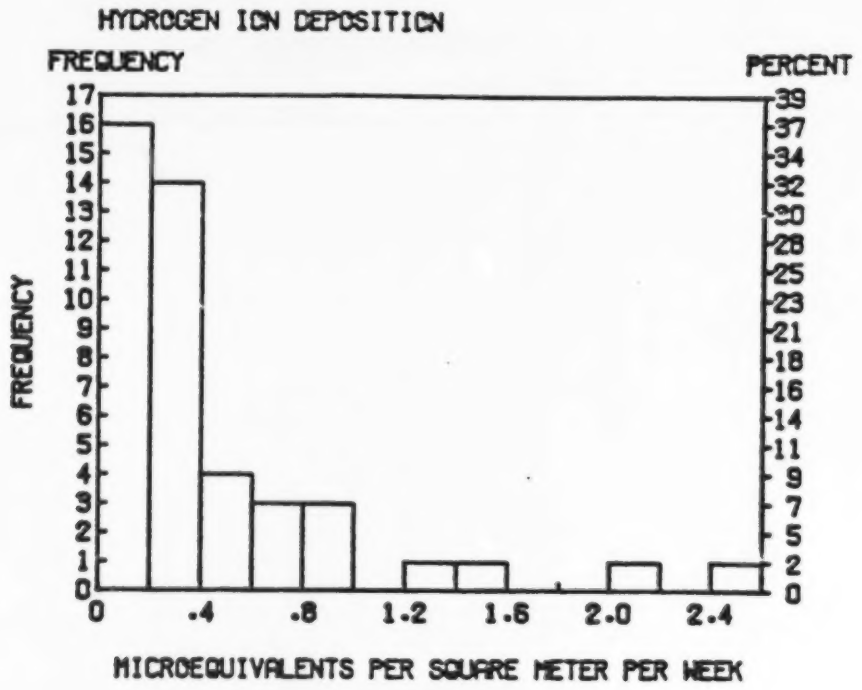

AMMONIUM ION DEPOSITION (CALCULATED AS N)
FREQUENCY
PERCENT
FREQUENCY
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
0 2 4 5 7 9 11 13 14 16 18 20 22 23 25 27
0 1.0 2.0 3.0 4.0 5.0 6.0
MG-N/SQUARE METER PER WEEK

FIGURE 21 : Frequency of Occurrence at Maple Leaf



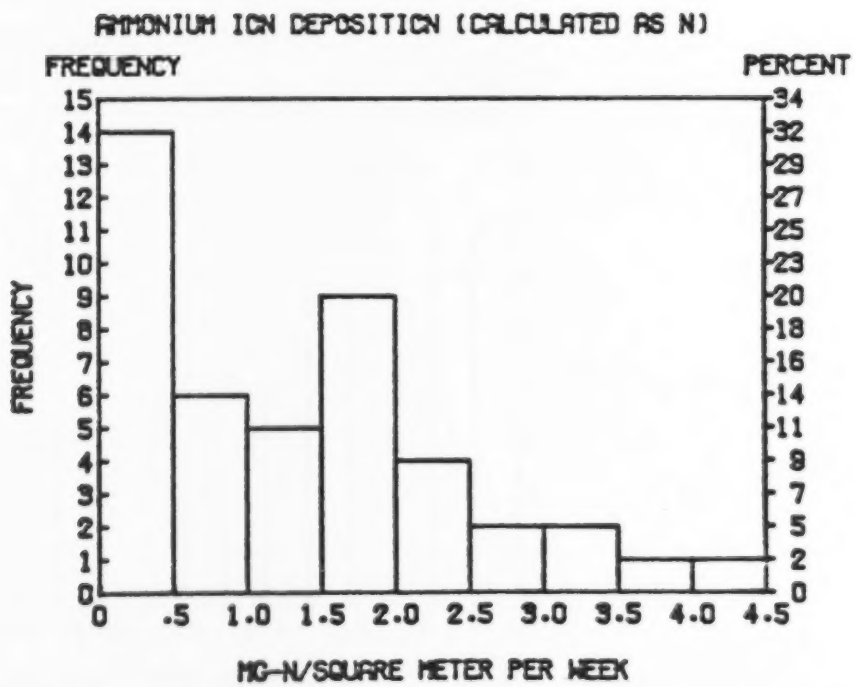
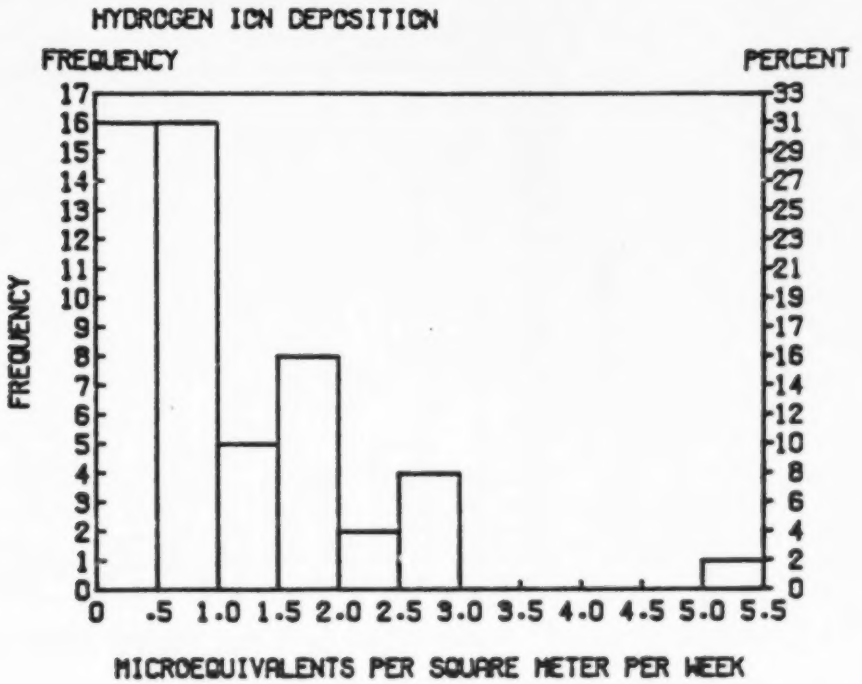


FIGURE 22 : Frequency of Occurrence atBellingham


HYDROGEN ION DEPOSITION
FREQUENCY
PERCENT
FREQUENCY
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
0 2 4 6 8 10 12 14 16 17 19 21 23 25 27 29 31 33
0 .5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5
MICROEQUIVALENTS PER SQUARE METER PER WEEK

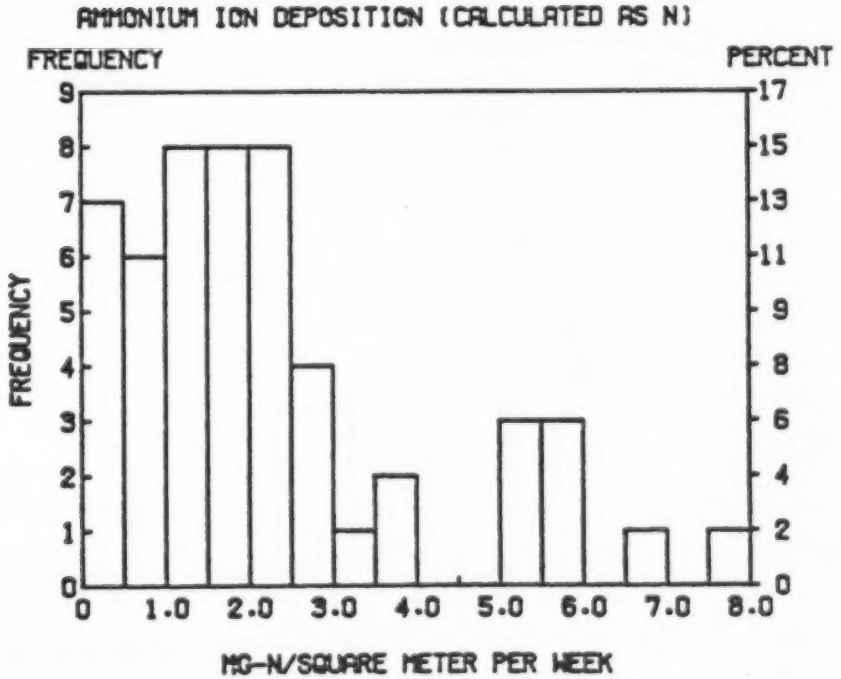
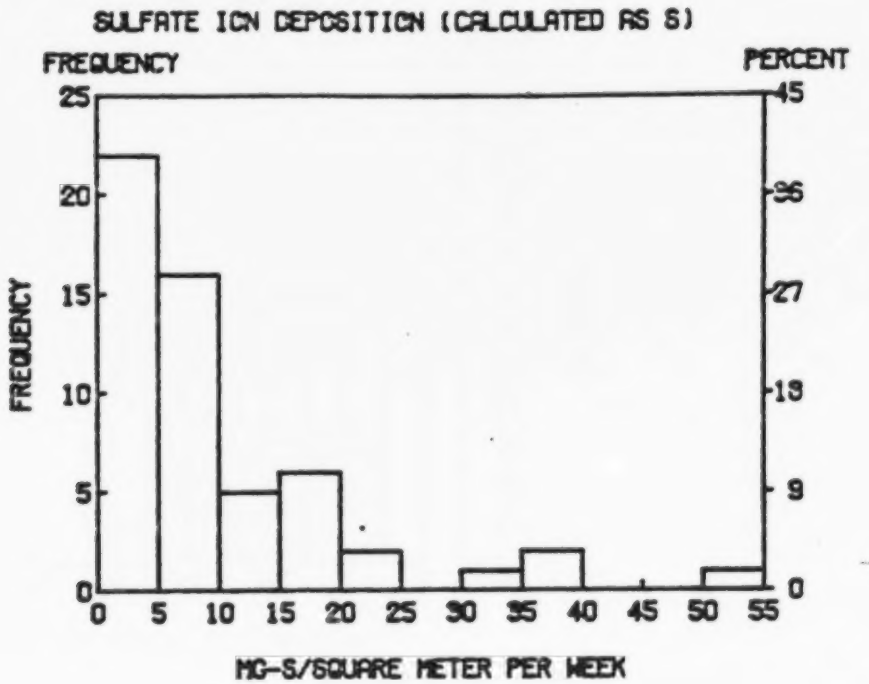

AMMONIUM ION DEPOSITION (CALCULATED AS N)
FREQUENCY
PERCENT
FREQUENCY
0 1 2 3 4 5 6 7 8 9
0 2 4 6 8 9 11 13 15 17
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0
MG-N/SQUARE METER PER WEEK

FIGURE 23 : Frequency of Occurrence at Tolt Reservoir



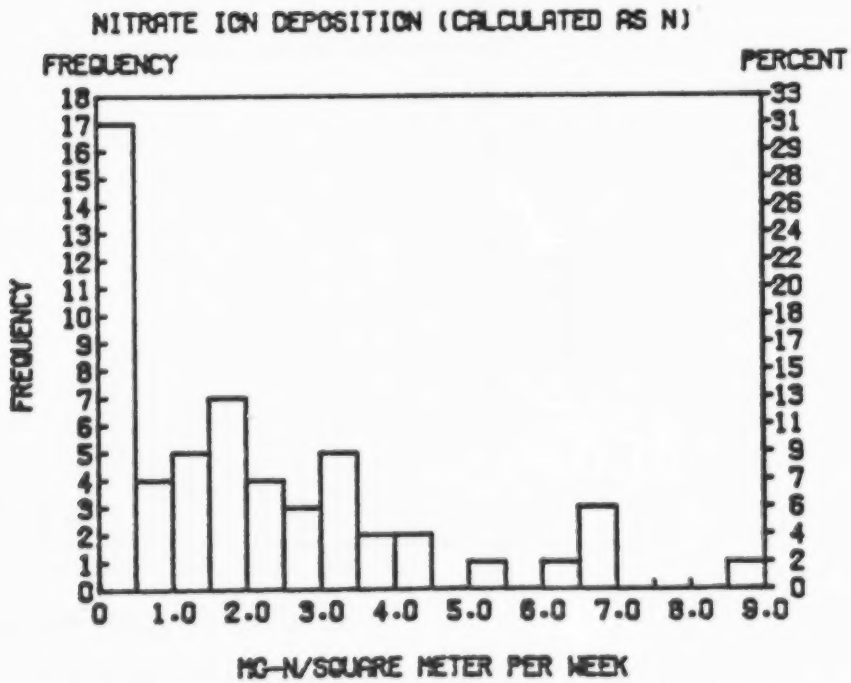
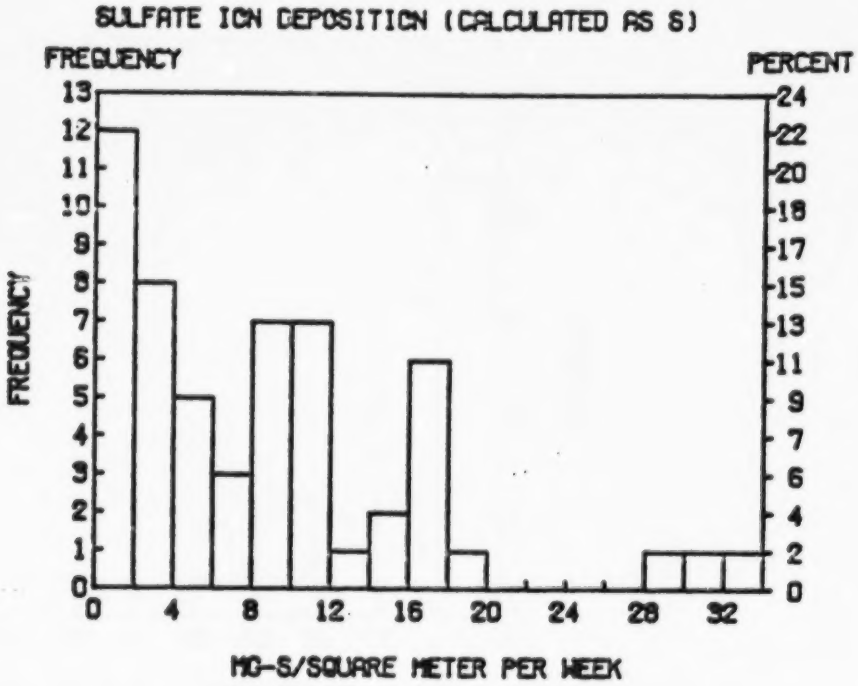


FIGURE 24 : Frequency of Occurrence at West Seattle


SULFATE ION DEPOSITION (CALCULATED AS S)
FREQUENCY
PERCENT
FREQUENCY
0 1 2 3 4 5 6 7 8 9 10 11 12 13
0 2 4 6 7 9 11 13 15 17 18 20 22 24
0 4 8 12 16 20 24 28 32
MG-S/SQUARE METER PER WEEK

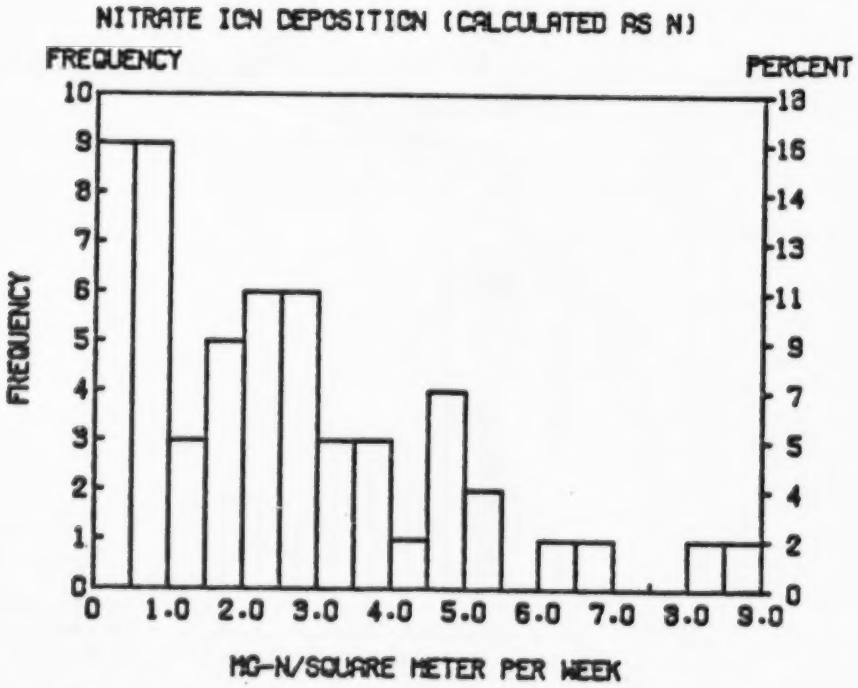
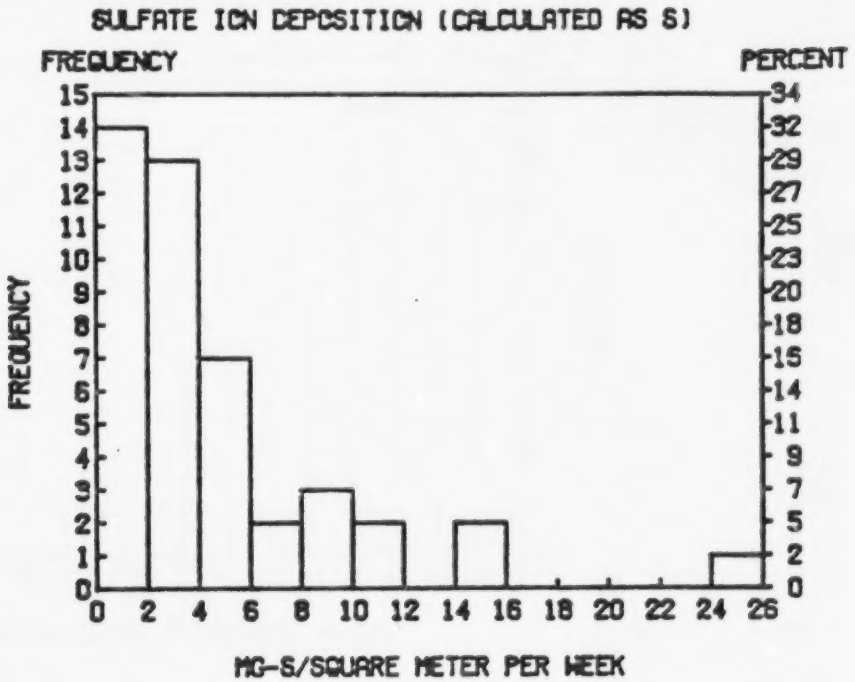

NITRATE ION DEPOSITION (CALCULATED AS N)
FREQUENCY
PERCENT
FREQUENCY
0 1 2 3 4 5 6 7 8 9 10
0 2 4 5 7 9 11 13 14 16 18
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0
MG-N/SQUARE METER PER WEEK

FIGURE 25 : Frequency of Occurrence at Maple Leaf


SULFATE ION DEPOSITION (CALCULATED AS S)
FREQUENCY
PERCENT
FREQUENCY
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15
0 2 5 7 9 11 14 16 18 20 23 25 27 29 32 34
0 2 4 6 8 10 12 14 16 18 20 22 24 26
MG-S/SQUARE METER PER WEEK

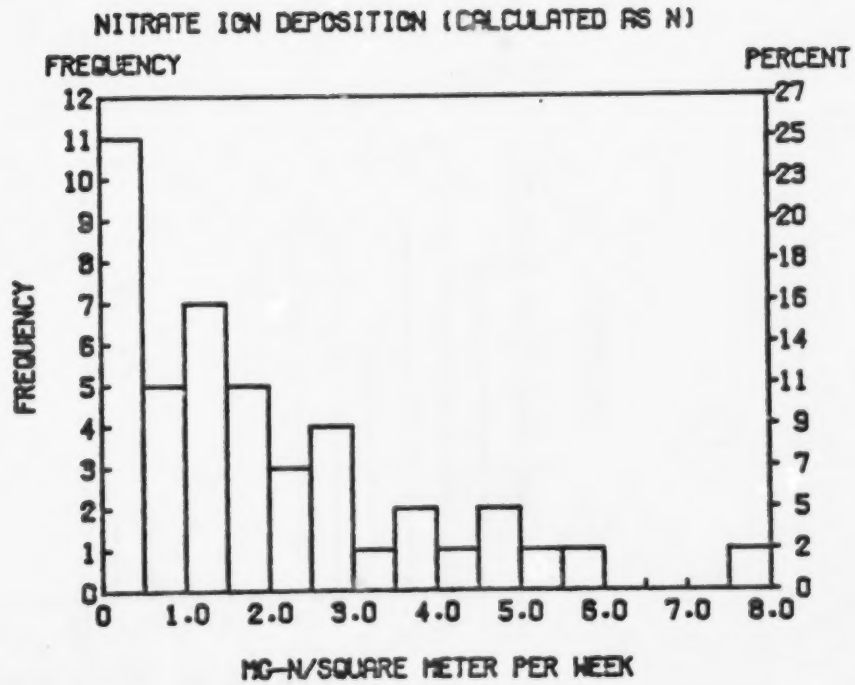
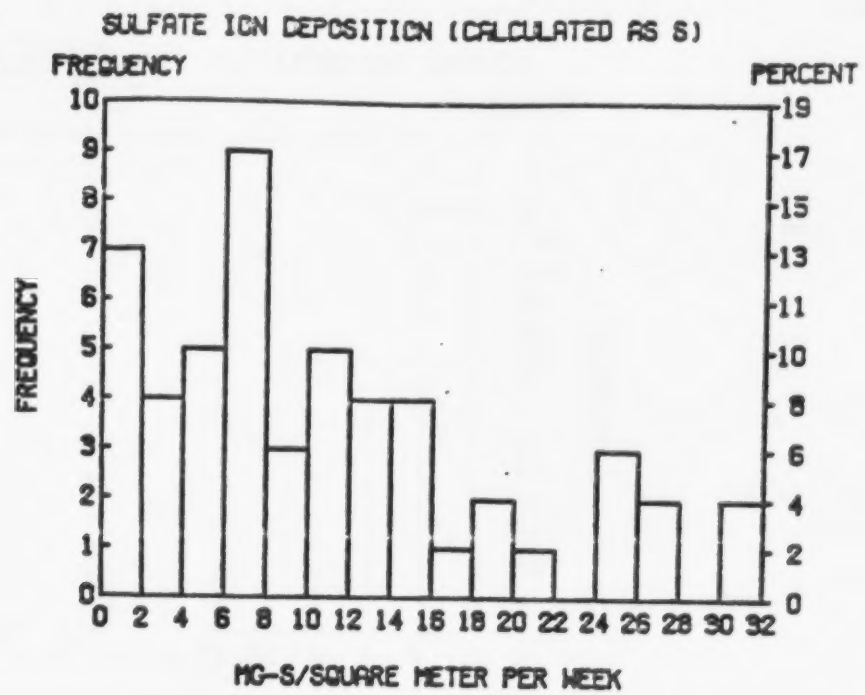

NITRATE ION DEPOSITION (CALCULATED AS N)
FREQUENCY
PERCENT
FREQUENCY
0 1 2 3 4 5 6 7 8 9 10 11 12
0 2 5 7 9 11 14 16 18 20 23 25 27
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0
MG-N/SQUARE METER PER WEEK

FIGURE 26 : Frequency of Occurrence at Bellingham


SULFATE ION DEPOSITION (CALCULATED AS S)
FREQUENCY
PERCENT
FREQUENCY
0 1 2 3 4 5 6 7 8 9 10
0 2 4 6 8 10 12 14 16 18 19
0 2 4 6 8 10 11 13 15 17 19
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32
MG-S/SQUARE METER PER WEEK

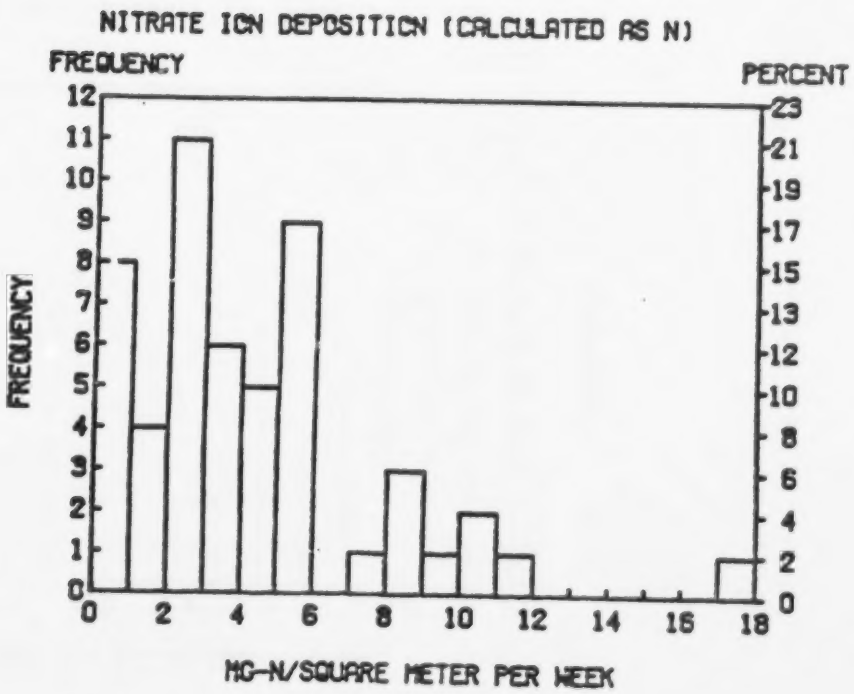

NITRATE ION DEPOSITION (CALCULATED AS N)
FREQUENCY
PERCENT
FREQUENCY
0 1 2 3 4 5 6 7 8 9 10 11 12
0 2 4 6 8 10 12 14 16 18 23
0 2 4 6 8 10 12 13 15 17 19 21 23
0 2 4 6 8 10 12 14 16 18
MG-N/SQUARE METER PER WEEK

FIGURE 27 : Frequency of Occurrence at Tolt Reservoir

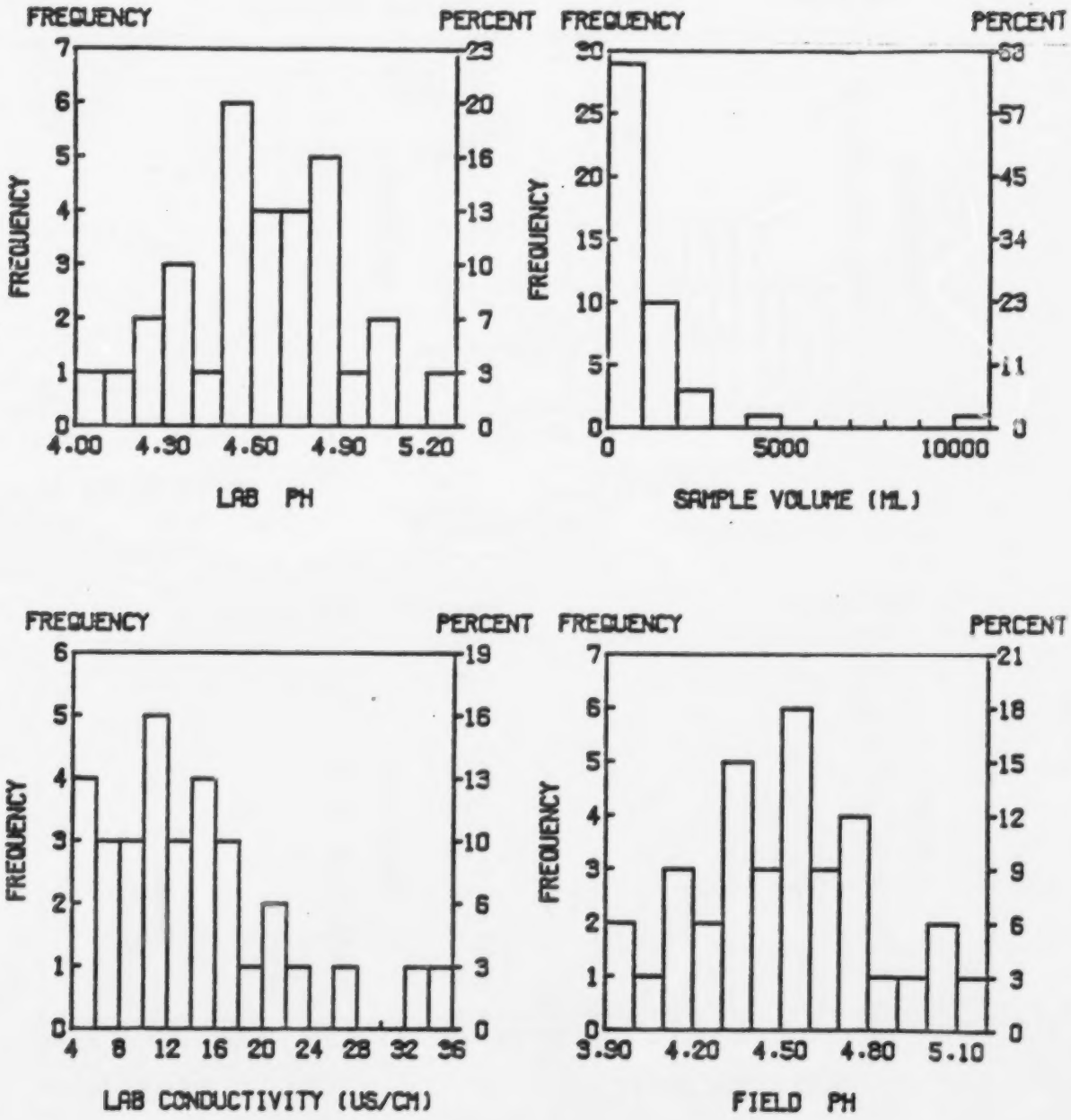


FIGURE 28 : Frequency of Occurrence at West Seattle

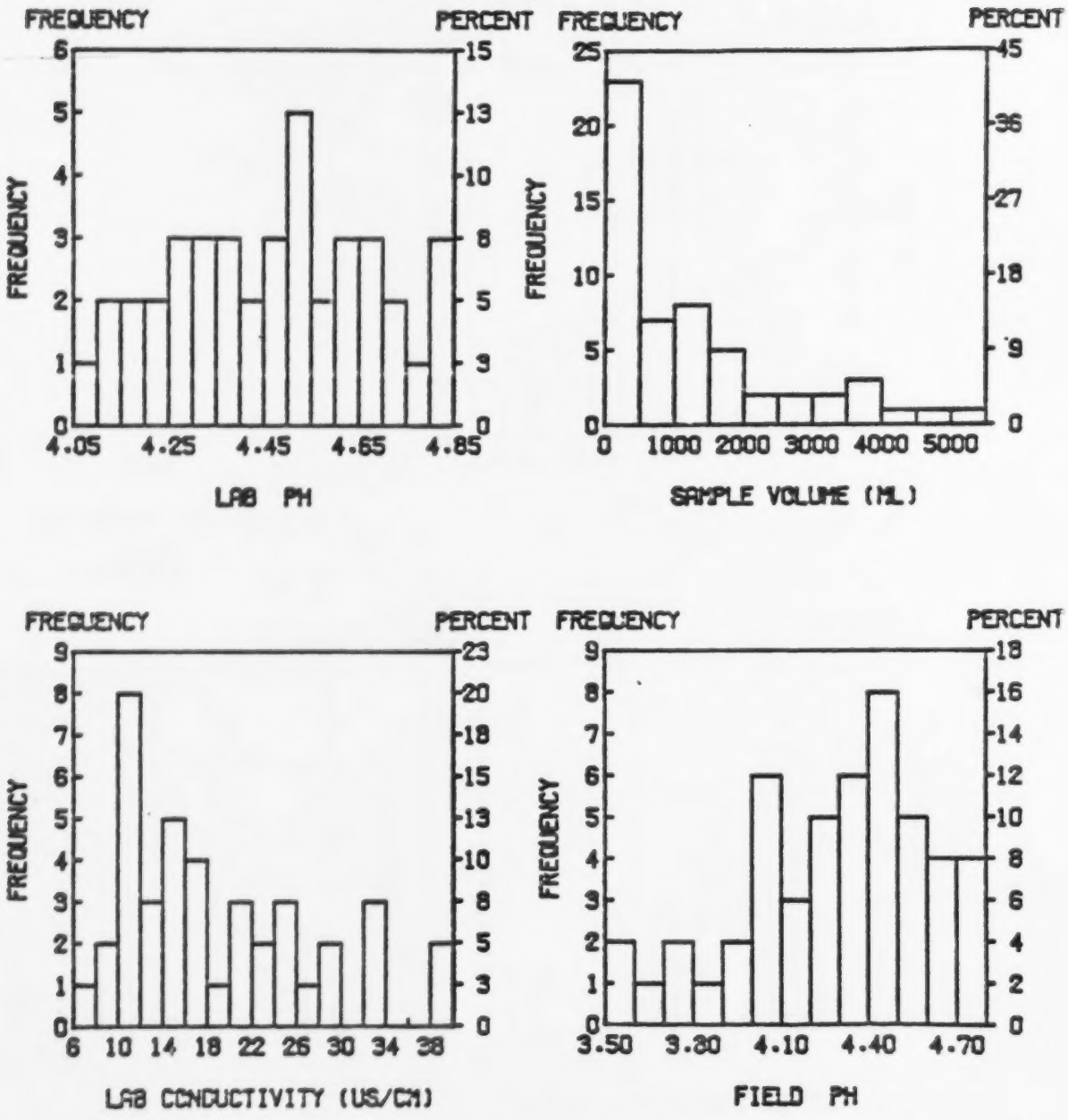


FIGURE 29 : Frequency of Occurrence at Maple Leaf

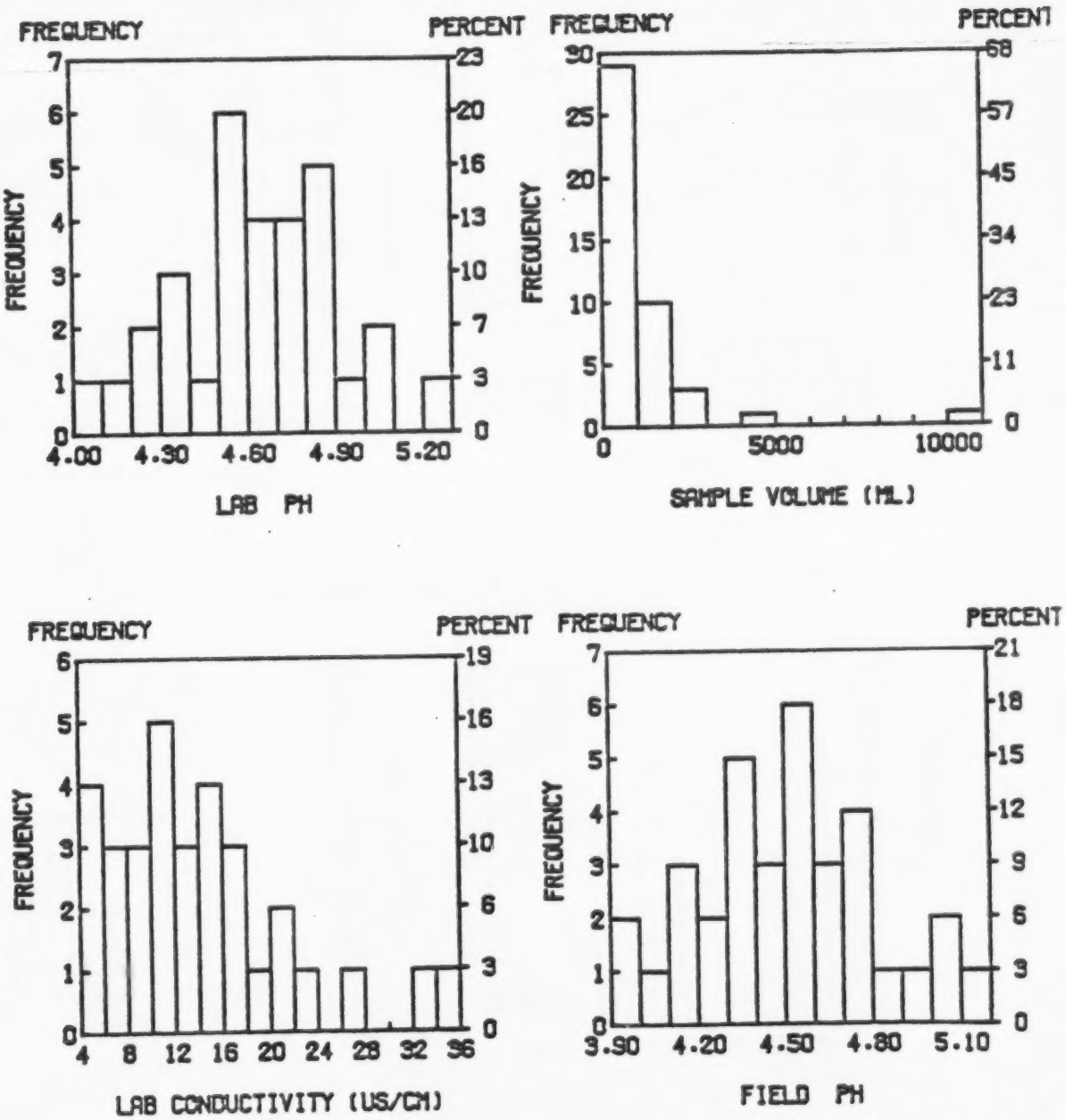


FIGURE 30 : Frequency of Occurrence at Bellingham

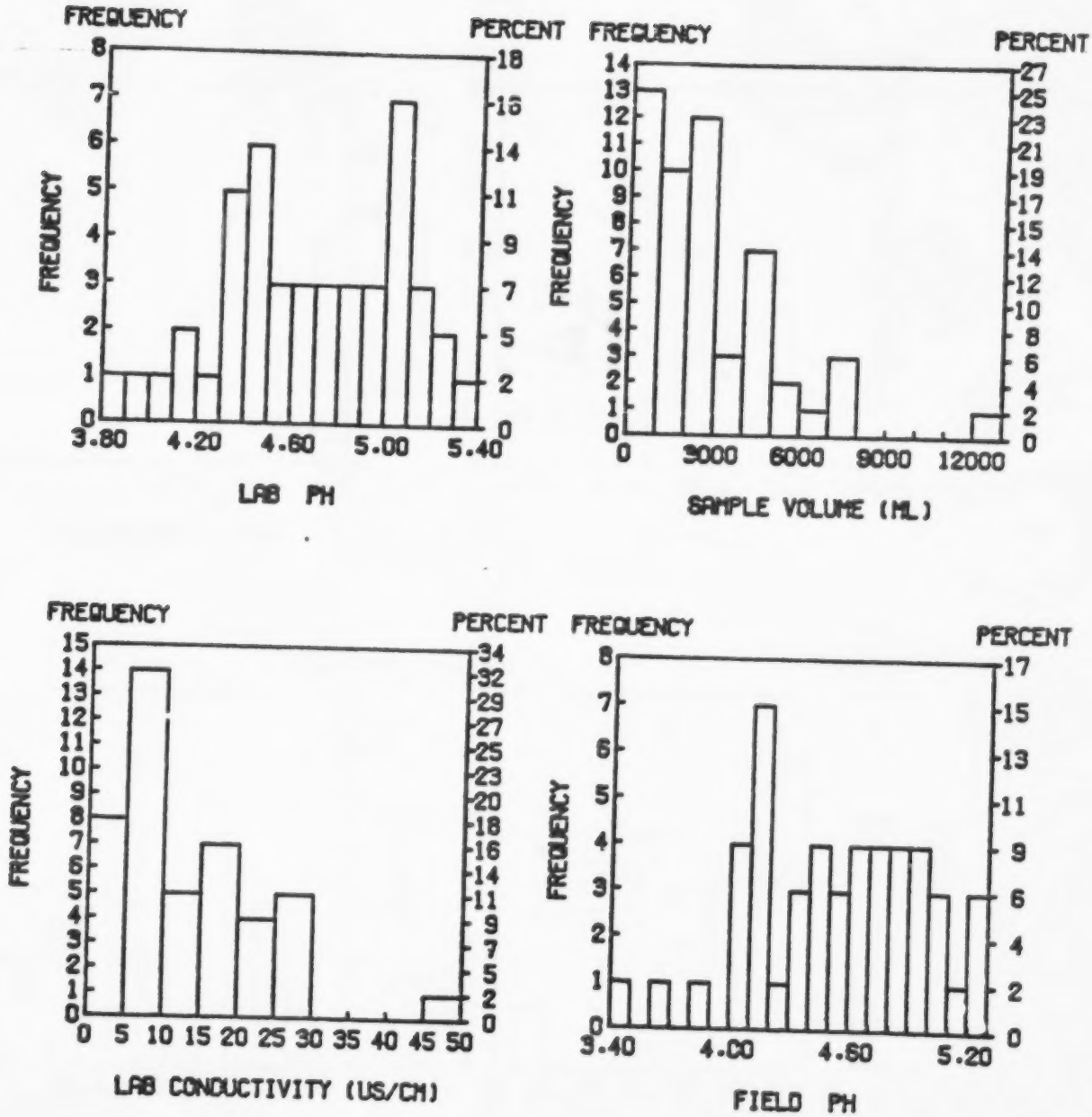


FIGURE 31 : Frequency of Occurrence at Tolt Reservoir

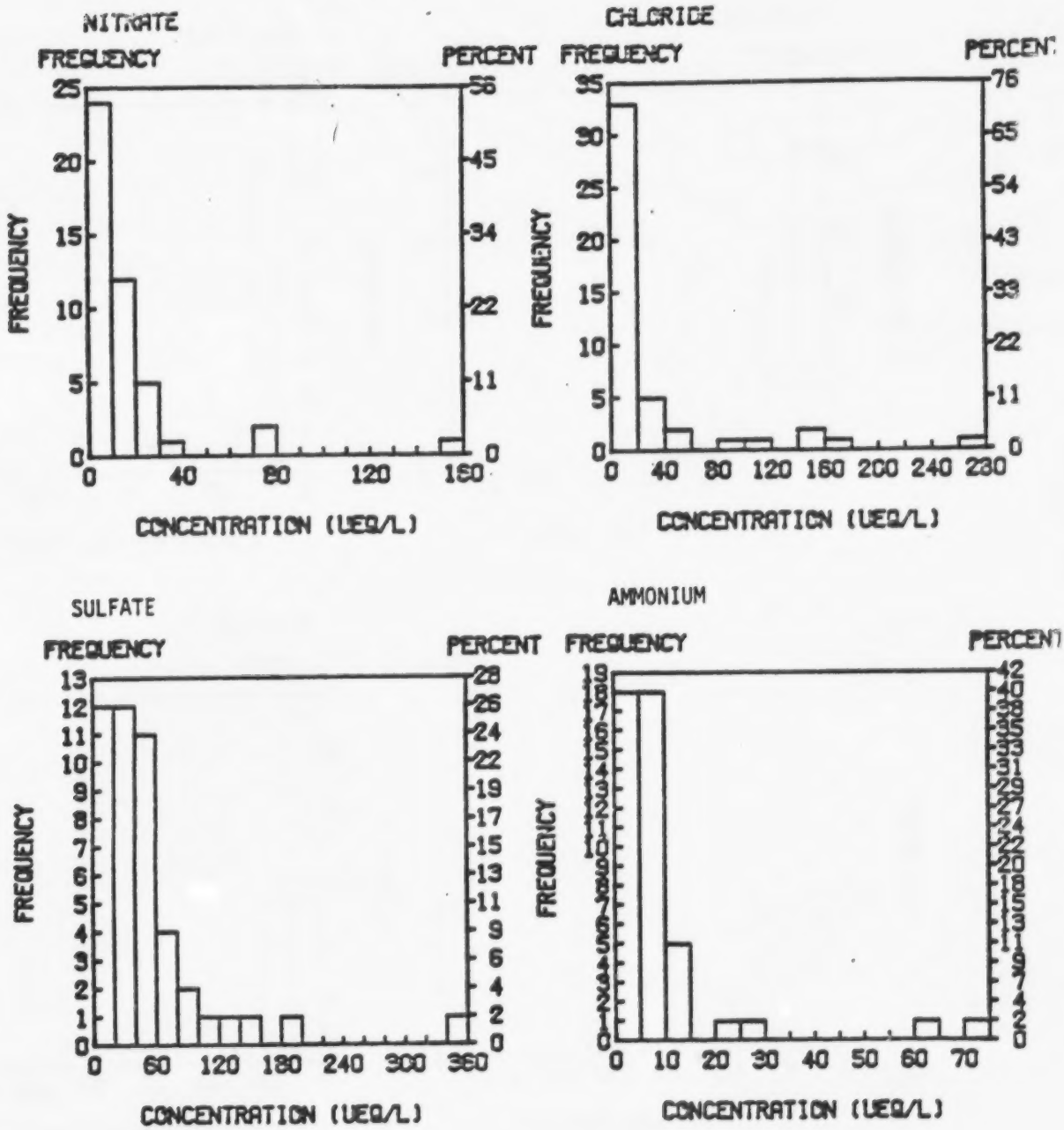


FIGURE 32 : Frequency of Occurrence at West Seattle

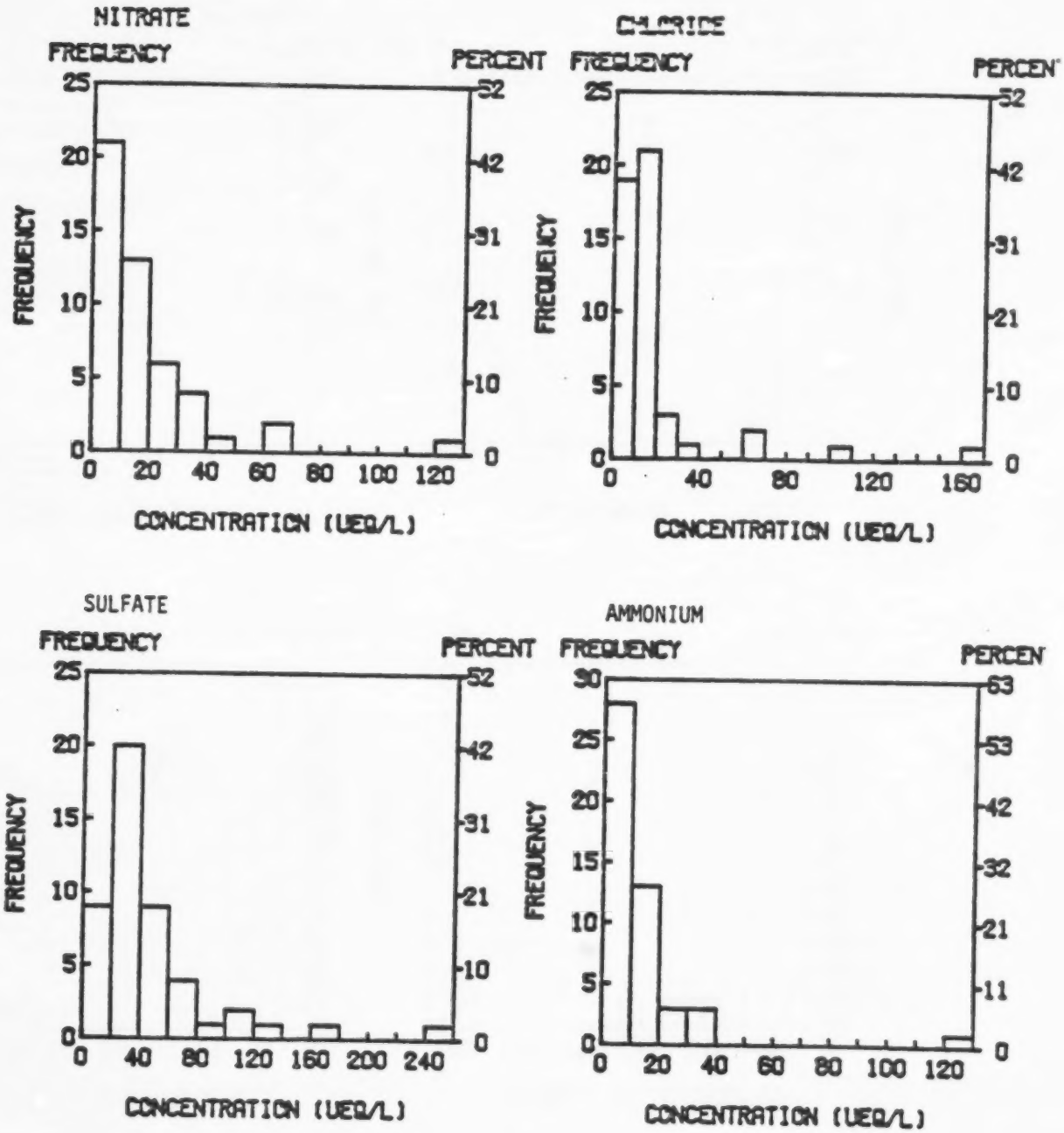


FIGURE 33 : Frequency of Occurrence at Maple Leaf

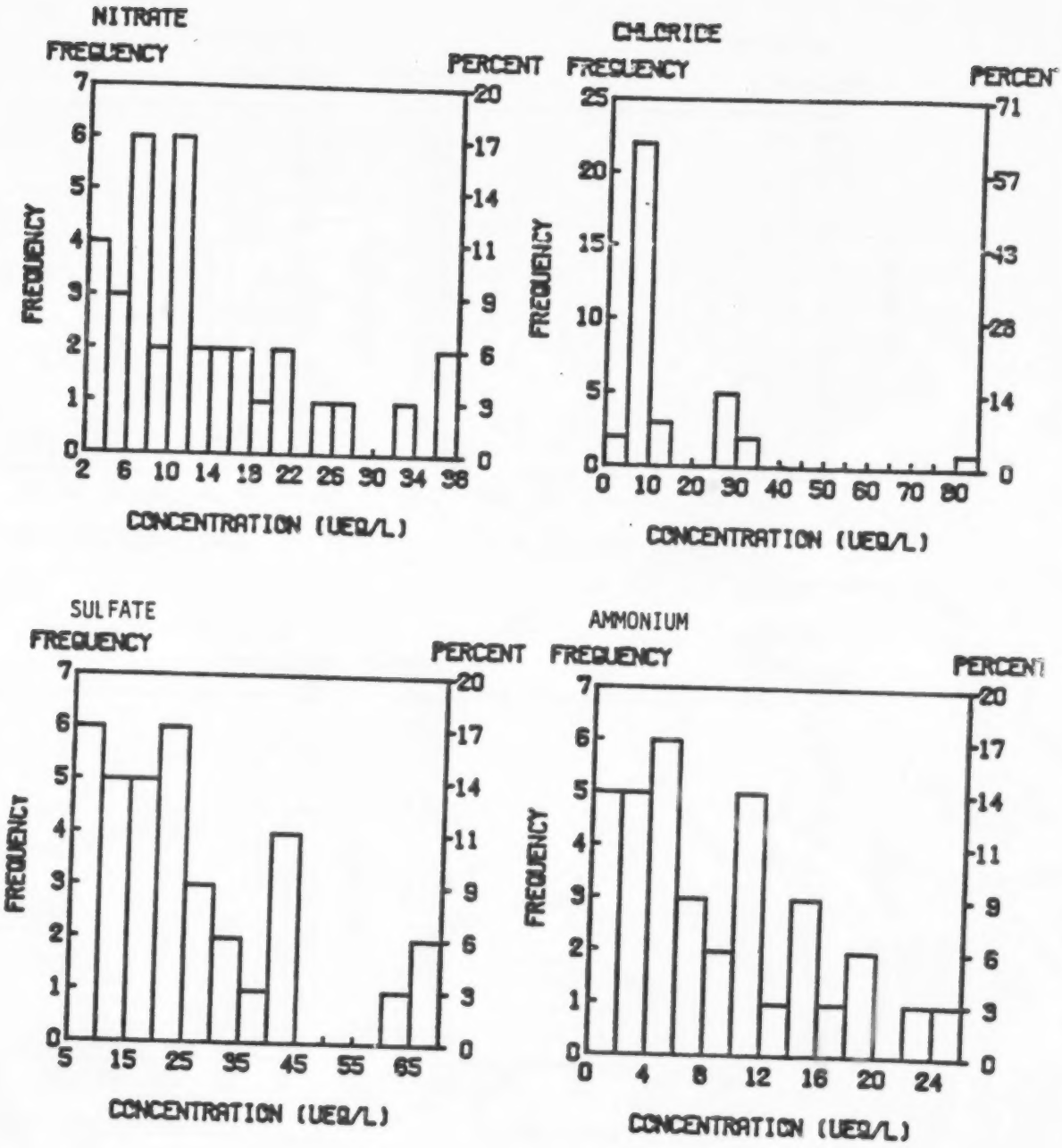


FIGURE 34 : Frequency of Occurrence at Bellingham

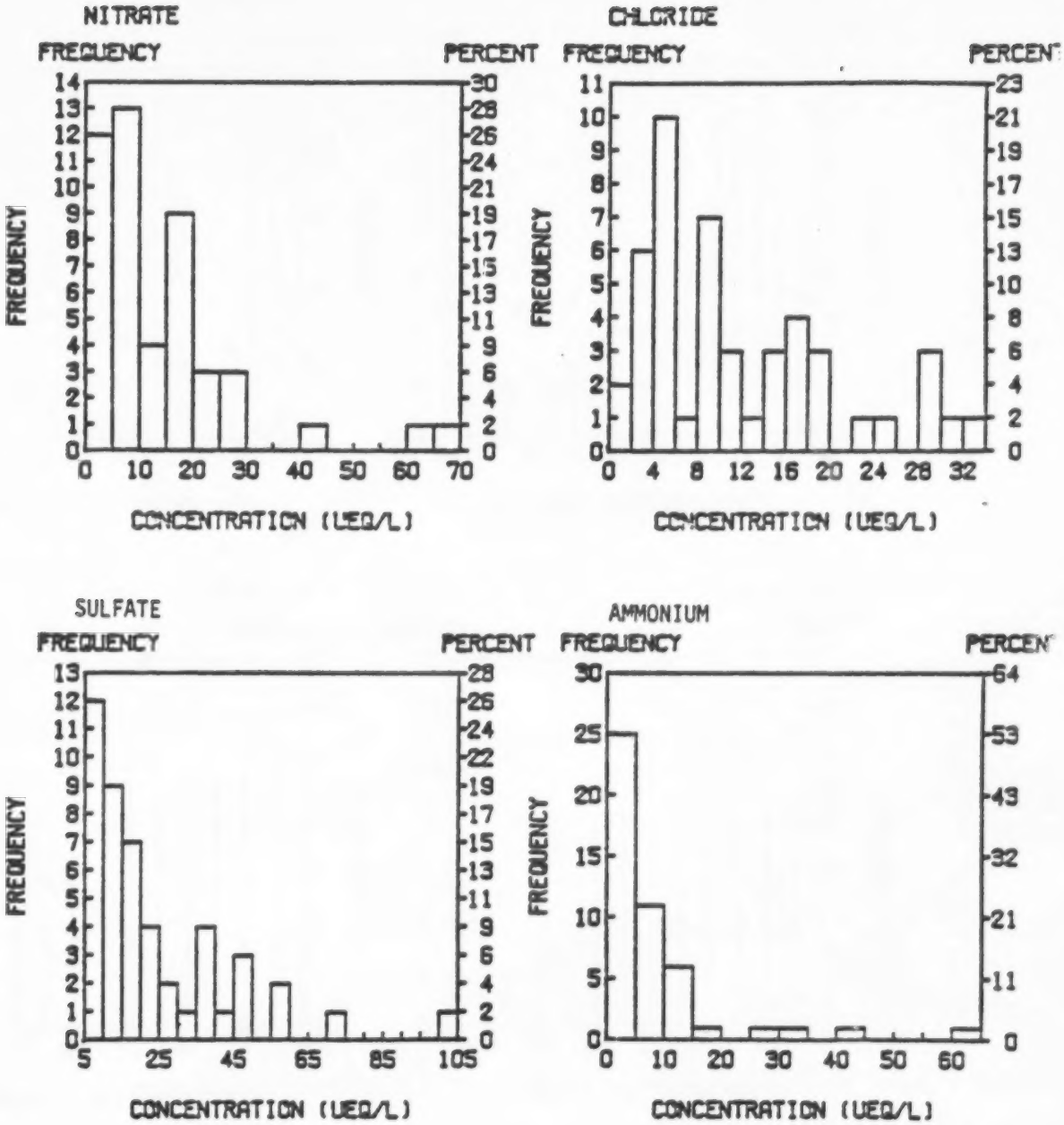


FIGURE 35 : Frequency of Occurrence at Tolt Reservoir

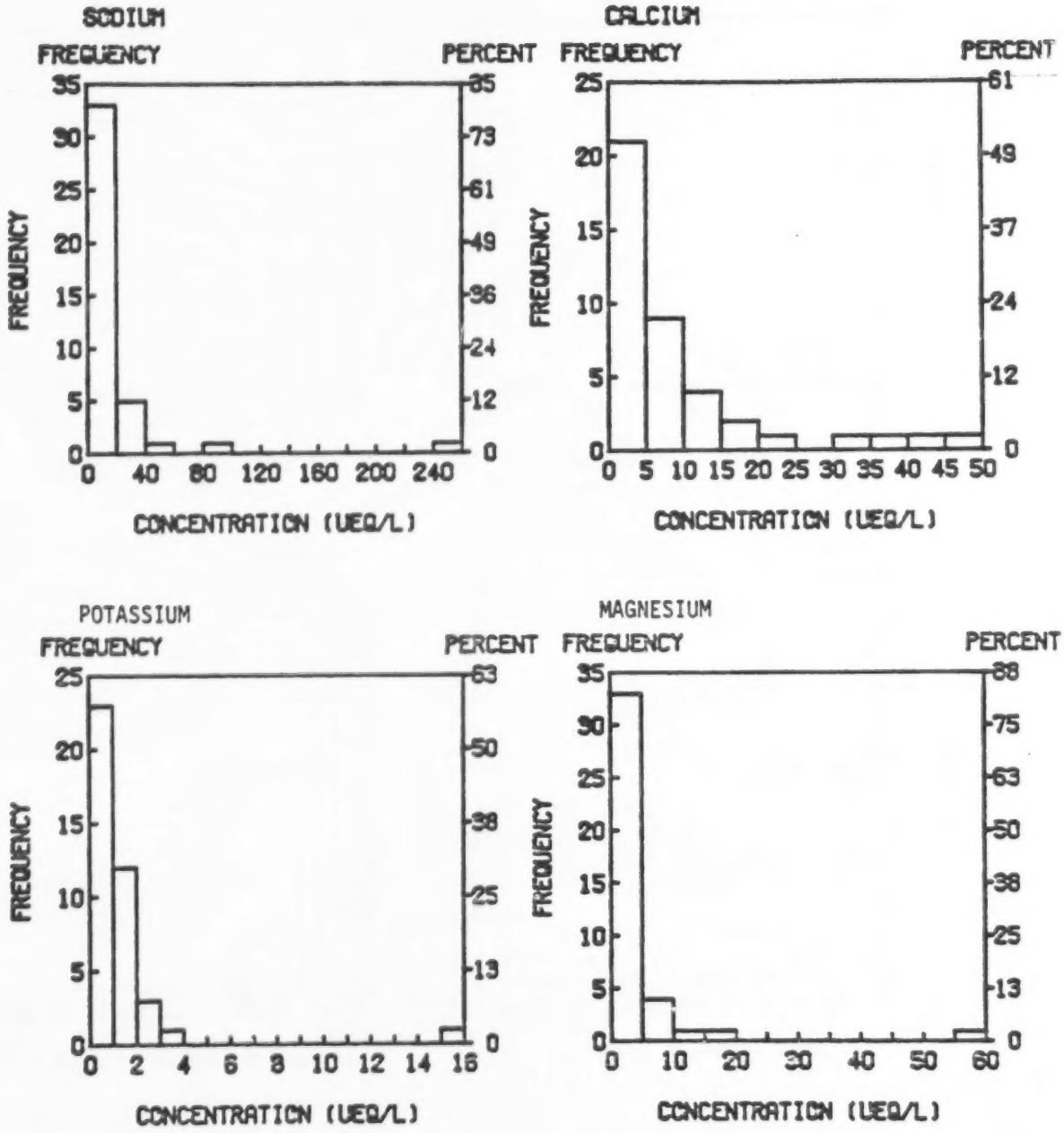


FIGURE 36 : Frequency of Occurrence at West Seattle

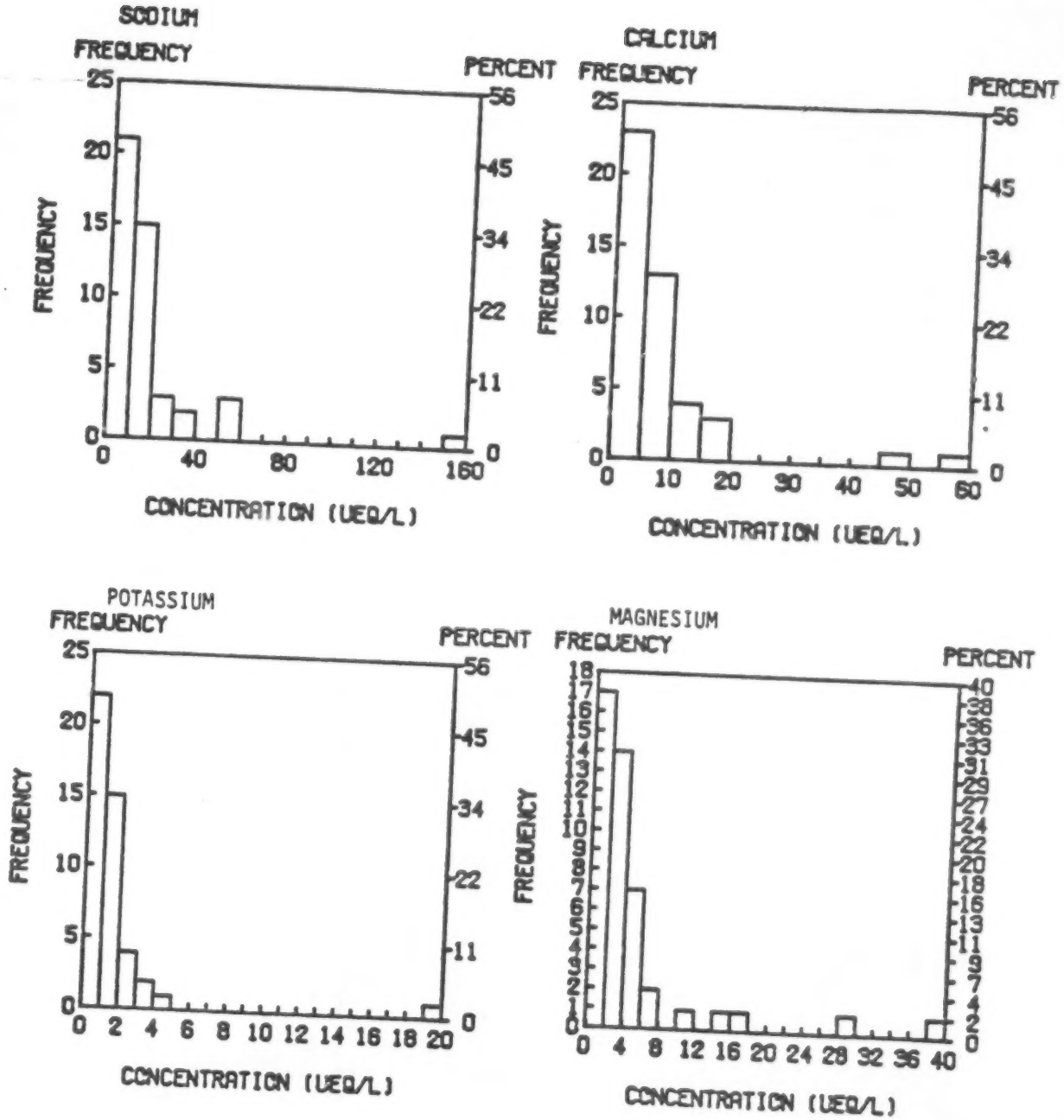


FIGURE 37 : Frequency of Occurrence at Maple Leaf

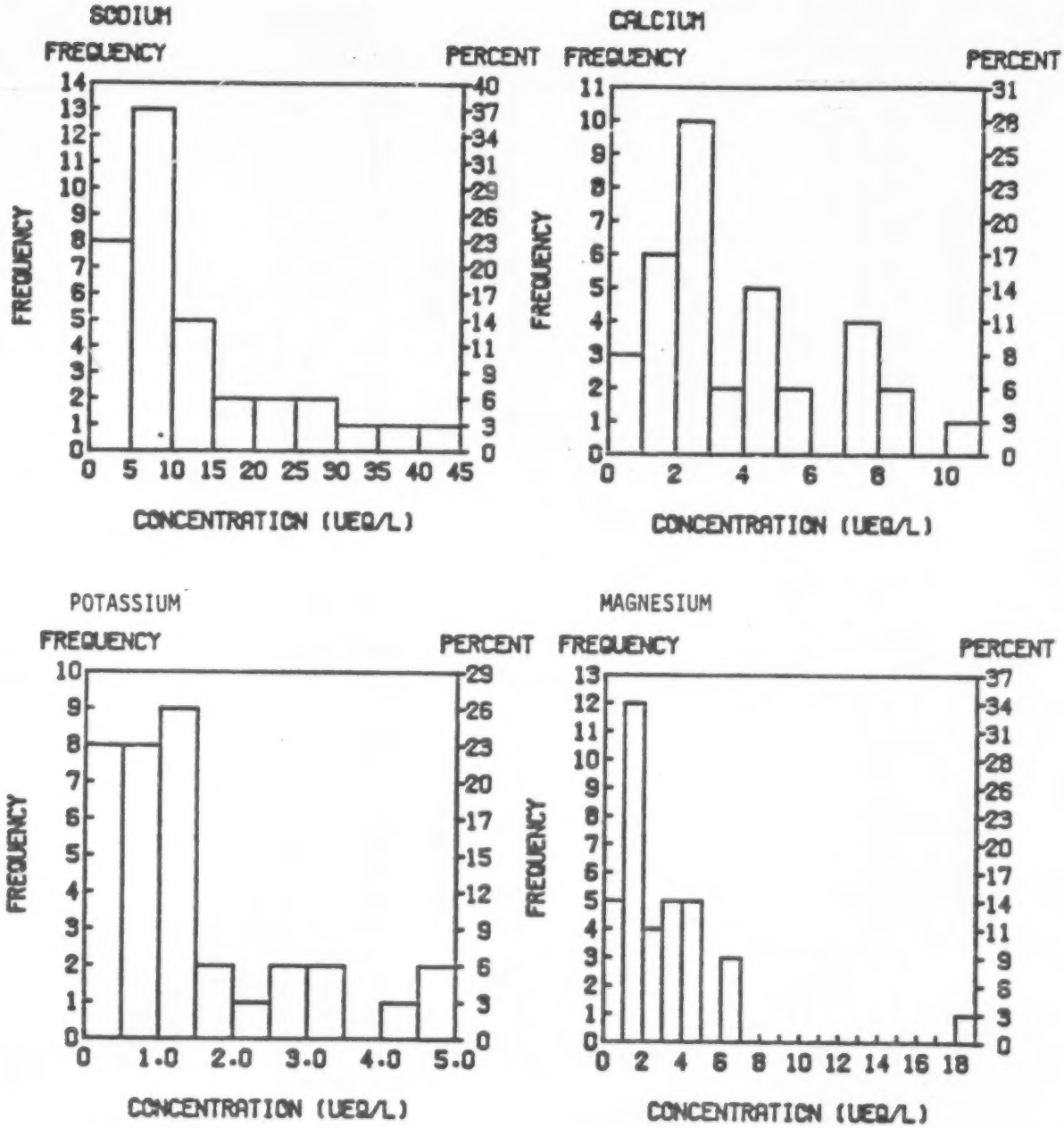


FIGURE 38 : Frequency of Occurrence at Bellingham

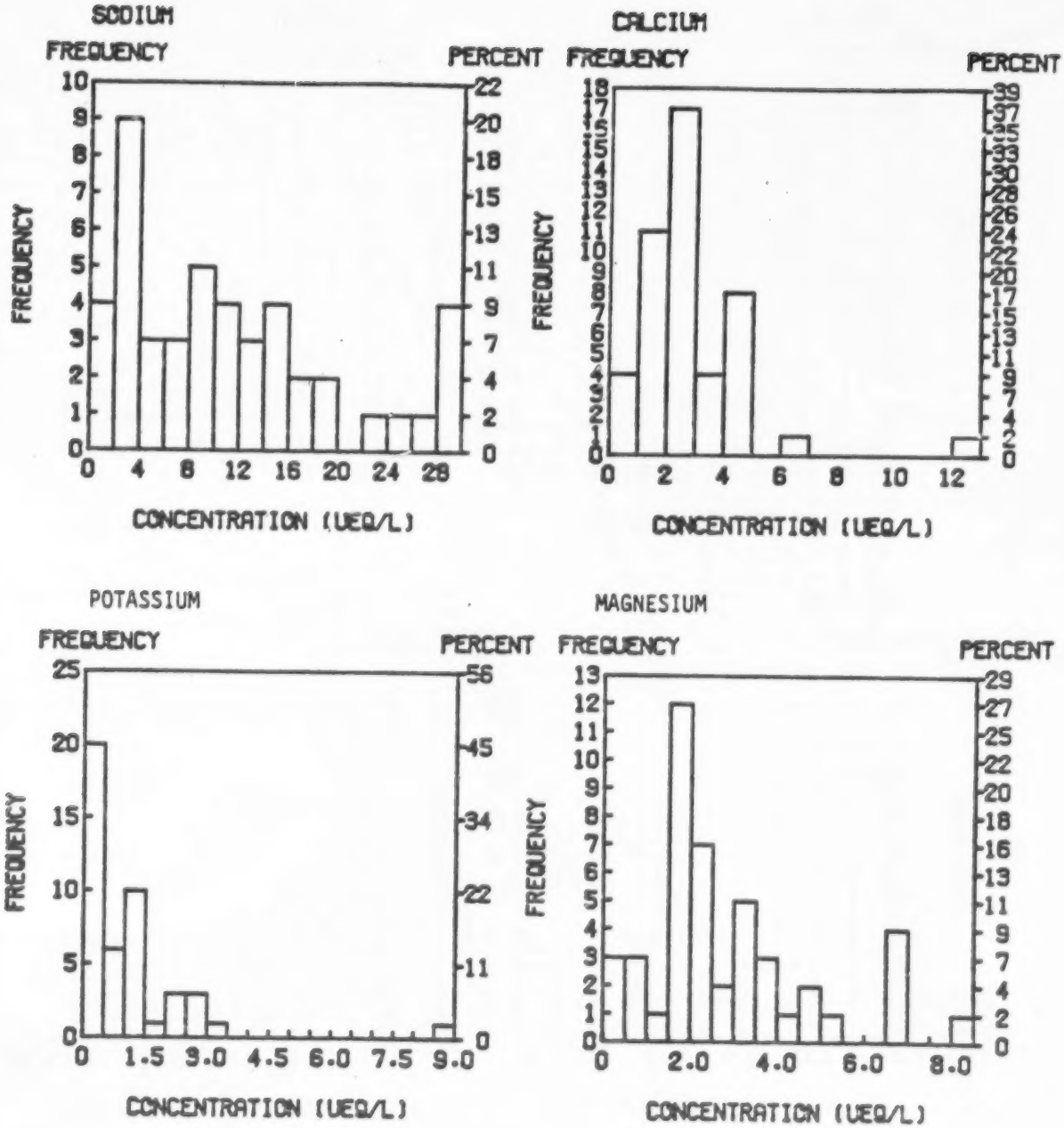


FIGURE 39 : Frequency of Occurrence at Toit Reservoir

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APPENDIX C

Pairwise Correlation Coefficients and Results of Factor Analysis

VARIMAX ROTATED FACTOR MATRIX
AFTER ROTATION WITH KAISER NORMALIZATION

	FACTOR 1	FACTOR 2	FACTOR 3	FACTOR 4
NH4	.74490	.25838	.35469	.38762
NO3	.87429	.20080	.25902	.16850
SO4XS	.80215	.29355	.35581	-.09453
AS	.00923	.19821	.70186	.18458
CU	.11144	-.00332	.28654	-.06442
PB	.49182	.31907	.73492	.12640
CA	.29146	.49963	.76917	-.13178
MG	.18813	.87375	.33789	-.12996
K	.55765	.47440	-.06237	.20350
CL	.14196	.93105	.26070	.00907
NA	.26484	.86653	.09543	.19158
HH	.85951	.06440	.14989	-.29935

FACTOR	EIGENVALUE	PCT OF VAR	CUM PCT
1	6.38554	68.2	68.2
2	1.55491	16.9	85.2
3	.97375	10.4	95.6
4	.41497	4.4	100.0

VARIABLE	COMMUNALITY
NH4	.89769
NO3	.90019
SO4XS	.86515
AS	.56605
CU	.09858
PB	.89976
CA	.94356
MG	.92988
K	.58133
CL	.95506
NA	.86682
HH	.85497

Factor Analysis Results

Maple Leaf

VARIMAX ROTATED FACTOR MATRIX
AFTER ROTATION WITH KAISER NORMALIZATION

	FACTOR 1	FACTOR 2	FACTOR 3	FACTOR 4
NH4	.90550	.01699	.10334	.21267
NO3	.53352	.00397	.11684	.15743
SO4XS	.85514	.00166	.00818	.28933
AS	.23385	.07485	.10362	.49262
CU	-.02187	-.17838	.32760	.18663
PB	.66849	.10521	.49634	.19562
CA	.47845	.16201	.26102	.65288
MG	.62440	.94956	-.00124	.08308
K	.48113	.13724	.80939	.08385
CL	-.67022	.99362	-.09992	.02763
NA	.06749	.79712	.04135	.07181
HH	.92389	-.03384	.22692	.13322

FACTOR	EIGENVALUE	PCT OF VAR	CUM PCT
1	5.22816	48.2	56.2
2	2.59864	23.9	87.2
3	.70977	7.9	95.1
4	.44012	4.9	100.0

VARIABLE	COMMUNALITY
NH4	.87612
NO3	.90990
SO4XS	.81534
AS	.31370
CU	.17445
PB	.74236
CA	.74955
MG	.90916
K	.91247
CL	1.00296
NA	.64633
HH	.92396

Tolt Reservoir

VARIMAX ROTATED FACTOR MATRIX
AFTER ROTATION WITH KAISER NORMALIZATION

	FACTOR 1	FACTOR 2	FACTOR 3	FACTOR 4	FACTOR 5
NH4	.01105	.83599	.10166	.11960	.16005
NO3	.02324	.95312	.10132	.26244	.13292
SO4XS	.13632	.35863	.16297	.87197	.12272
AS	.10768	.02161	.76041	.03004	-.02005
CU	.03539	.18879	.03947	.06644	.78164
PB	.06877	.41379	.84279	.22981	.23966
CA	.17761	.50333	.31327	.12503	.36830
MG	.94548	.05491	.12273	.09647	-.07327
K	.07857	.19392	.03127	.39940	.21313
CL	.95418	-.05142	.04471	-.08393	.09654
NA	.94407	.04067	.09452	.03295	.03811
HH	.06208	.20848	.11401	.82751	.04672

FACTOR	EIGENVALUE	PCT OF VAR	CUM PCT
1	4.49237	47.2	47.2
2	2.68542	28.2	75.4
3	1.00192	10.5	85.9
4	.70523	7.4	93.3
5	.63446	6.7	100.0

VARIABLE	COMMUNALITY
NH4	.74926
NO3	1.00579
SO4XS	.77414
AS	.59159
CU	.65393
PB	.99649
CA	.53430
MG	.92668
K	.70398
CL	.93147
NA	.90461
HH	.74727

West Seattle

VARIMAX ROTATED FACTOR MATRIX
AFTER ROTATION WITH KAISER NORMALIZATION

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	FACTOR 1	FACTOR 2	FACTOR 3	FACTOR 4	FACTOR 5
NH4	-.03988	.87193	.23614	.07096	.17369
NO3	.66351	.73406	.44187	.49263	.02269
SO4XS	-.01443	.36760	.30169	.55210	.43524
AS	.16126	-.06743	.05295	.04303	.43033
CU	.11472	.49270	.00075	.11932	-.17460
PB	-.08819	.22533	.84304	.19347	.03271
CA	.16500	.45393	.28463	.21273	.46083
MG	.93370	.00422	.05796	-.00164	.18325
K	.16395	.09643	.76683	.12937	.19244
CL	.99646	.03746	-.03063	-.08596	.06179
NA	.86345	.13365	.06130	.09549	.12336
HH	-.02767	.35436	.47424	.62820	.10228

FACTOR	EIGENVALUE	PCT.OF VAR	CUM PCT
1	4.33529	50.4	50.4
2	2.67514	31.1	81.5
3	.83112	9.7	91.2
4	.47408	5.5	96.7
5	.28278	3.3	100.0

VARIABLE	COMMUNALITY
NH4	.85377
NO3	.98132
SO4XS	.72060
AS	.22039
CU	.30063
PB	.80822
CA	.57199
MG	.90875
K	.67798
CL	1.00647
NA	.79202
HH	.75634

Bellingham

Pairwise Correlation Coefficients

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	MG4	MN3	FE	SIM	AS	CU	PB	K	NA	NG
MN4	1.00000	.94936	.79840	.90947	.74712	.42034	.94315	.94043	.86310	.77279
MN3	.94936	1.00000	.74477	.94073	.66419	.47002	.85347	.88019	.88907	.73320
FE	.79840	.74477	1.00000	.77585	.74752	.39499	.86437	.83696	.96460	.98480
SIM	.90947	.94073	.77585	1.00000	.69196	.47469	.84676	.81578	.81821	.78526
AS	.74712	.66419	.74752	.69108	1.00000	.51730	.80117	.68786	.76609	.72355
CU	.42034	.47002	.38499	.42462	.41730	1.00000	.41962	.40557	.37231	.37243
PB	.94315	.85347	.86437	.84676	.80117	.41962	1.00000	.92970	.88837	.85477
K	.94043	.88019	.83496	.81578	.68786	.40557	.92970	1.00000	.89583	.80648
NA	.86310	.88907	.96460	.81821	.76609	.37231	.88837	.89583	1.00000	.93806
NG	.77279	.73320	.98480	.78526	.72355	.37243	.85477	.80648	.93806	1.00000
CA	.79647	.73811	.86528	.80522	.74035	.42099	.89893	.78819	.81265	.88952
VNL	-.35178	-.42908	-.30494	-.40487	-.14808	-.09596	-.30847	-.41291	-.34413	-.33700
IRI	.75109	.86627	.94056	.89057	.43079	.36138	.86281	.85612	.80648	.97938

	CA	VNL	IRI
MN4	.79647	-.35178	.75109
MN3	.73811	-.42908	.86627
FE	.86528	-.30494	.94056
SIM	.80522	-.40487	.89057
AS	.74035	-.14808	.43079
CU	.42099	-.09596	.36138
PB	.89893	-.30847	.86281
K	.78819	-.41291	.85612
NA	.81265	-.34413	.80648
NG	.88952	-.33700	.97938
CA	1.00000	-.34459	.80648
VNL	-.34459	1.00000	-.52410
IRI	.80648	-.52410	1.00000

Maple Leaf

97

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	MIN	MD	CL	SOL	AS	CU	PB	K	MA	MG
MIN	1.00000	.78581	-.05851	.31163	.02089	.26358	.61382	.83518	-.02671	.00026
MD	.78581	1.00000	.30366	.66674	.08893	.75187	.32935	.44458	.34351	.39077
CL	-.05851	.30366	1.00000	.43564	.33303	.17705	.61565	.92637	.98766	.98600
SOL	.31163	.66674	.43564	1.00000	.21973	.61292	.61117	.56433	.43992	.51457
AS	.02089	.08893	.33303	.21973	1.00000	.36083	.19038	.46156	.53666	.50680
CU	.26358	.26187	.17705	.61292	.36083	1.00000	.62812	.22730	.19384	.19102
PB	.61382	.32935	.61565	.61117	.59058	.62812	1.00000	.47296	.44109	.43769
K	.83518	.44458	.92637	.56433	.46156	.22730	.47296	1.00000	.95163	.94981
MA	-.02671	.34351	.98766	.43992	.53666	.19384	.44109	.95163	1.00000	.98379
MG	.00026	.39077	.98600	.51457	.50680	.19102	.43769	.94981	.98379	1.00000
CA	.37494	.62462	.46577	.61139	.36118	.50783	.78695	.56630	.59721	.53292
VOL	-.36946	-.67694	-.13829	-.39922	-.08720	-.17111	-.37142	-.28594	-.28664	-.26465
PH	.21690	.54020	.21729	.78575	-.00832	.35963	.35954	.37949	.26762	.29361

	CA	VOL	PH
MIN	.37494	-.36946	.21690
MD	.62462	-.67694	.54020
CL	.46577	-.13829	.21729
SOL	.61139	-.39922	.78575
AS	.36118	-.08720	-.00832
CU	.50783	-.17111	.35963
PB	.78695	-.37142	.35954
K	.56630	-.28594	.37949
MA	.59721	-.28664	.26762
MG	.53292	-.26465	.29361
CA	1.00000	-.38873	.27861
VOL	-.38873	1.00000	-.39964
PH	.27861	-.39964	1.00000

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86

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	NH4	NO3	CL	SO4	AS	CU	PB	K	NA	MG
NH4	1.00000	.70389	-.11984	.42717	-.08310	.28062	.33986	.27293	-.10369	-.10034
NO3	.70389	1.00000	-.07779	.08072	.02804	.44037	.34728	.52796	-.00155	.05937
CL	-.11984	-.07779	1.00000	-.04650	.02699	-.07349	-.21043	.14662	.00377	.95138
SO4	.42717	.08072	-.04650	1.00000	.22872	.14144	.42221	.40787	.04910	.11312
AS	-.08310	.02804	.02699	.22872	1.00000	-.06950	.47402	.20253	.12293	.09528
CU	.28062	.44037	-.07349	.14144	-.06950	1.00000	.41987	.08258	.14691	.02449
PB	.33986	.34728	-.21043	.42221	.47402	.41987	1.00000	.47369	-.19272	-.07948
K	.27293	.52796	.14662	.40787	.20253	.08258	.47369	1.00000	.15042	.24171
NA	-.10369	-.00155	.00377	.04910	.12293	.14691	-.19272	.15042	1.00000	.03259
MG	-.10034	.05937	.95138	.11312	.09528	.02449	-.07948	.24171	.03259	1.00000
CA	.44089	.15493	.11826	.33136	.26363	.04736	.29065	.49099	.16397	.29301
VOL	-.40907	-.39910	-.09414	-.39221	-.10713	-.12939	-.25881	-.25181	-.18441	-.13117
IPI	.39369	.81063	-.18417	.65303	.13079	.19039	.59402	.54719	-.11830	-.01194

	CA	VOL	IPI
NH4	.44089	-.40907	.39369
NO3	.15493	-.39910	.81063
CL	.11826	-.09414	-.18417
SO4	.33136	-.39221	.65303
AS	.26363	-.10713	.13079
CU	.04736	-.12939	.19039
PB	.29065	-.25881	.59402
K	.49099	-.25181	.54719
NA	.16397	-.18441	-.11830
MG	.29301	-.13117	-.01194
CA	1.00000	-.34895	.29301
VOL	-.34895	1.00000	-.32679
IPI	.29301	-.32679	1.00000

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99

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	NH4	NO3	CL	SO4	AS	CU	PB	K	MA	MG
NH4	1.00000	.96377	-.09213	.73747	.19133	.29879	.07487	.01769	.04984	.19613
NO3	.96377	1.00000	-.08115	.75762	.14231	.27214	.06010	.01702	.01573	.13566
CL	-.09213	-.08115	1.00000	-.02764	-.04768	-.06994	-.20316	.07435	.05857	.03394	.91242
SO4	.73747	.75762	-.02764	1.00000	.25549	.14145	.34031	.34031	.34031	.10709	.16848
AS	.19133	.14231	.06994	.25549	1.00000	.29916	.39923	.32426	.13479	.18640
CU	.29879	.27214	-.04516	.14145	.29916	1.00000	.42487	.73394	.08154	.00230
PB	.07487	.06010	.07435	.34031	.39923	.42487	1.00000	.72951	.10720	.25791
K	.01769	.01702	.05857	.34031	.13479	.73394	.72951	1.00000	.16886	.10193
MA	.04984	.01573	.03394	.10709	.18640	.08154	.10720	.16886	1.00000	.77340
MG	.19613	.13566	.91242	.16848	.18640	.00230	.25791	.10193	.77340	1.00000
CA	.06834	.06016	.09624	.04768	.47952	.43009	.69528	.01187	.10776	-.29324
VOL	-.12546	-.13150	.02187	-.46641	-.27112	-.16187	-.30985	-.26635	-.11394	-.02667
PH	.02517	.06788	-.08744	.08692	.22678	.27572	.75694	.54757	.01567	.11186

	CA	VOL	PH
NH4	.06834	-.12546	.02517
NO3	.06016	-.13150	.06788
CL	.09624	.02187	-.08744
SO4	.04768	-.46641	.08692
AS	.47952	-.27112	.22678
CU	.43009	-.16187	.27572
PB	.69528	-.30985	.75694
K	.01187	-.26635	.54757
MA	.10776	-.11394	.01567
MG	-.29324	-.02667	.11186
CA	1.00000	-.19522	.67706
VOL	-.19522	1.00000	-.00026
PH	.67706	-.00026	1.00000

Tolt
Reservoir

091

Appendix D

Excess Cation Concentrations (mg/l) (based on Cl-) *52 weeks

Bellingham

Volume Weighted Average	Linear Average
Na (-.001)	Nax .02
Mg .004	Mgx .006
K .028	Kx .045
Ca .043	Cax .068

West Seattle *

Volume Weighted Average	Linear Average
Na -.067	-.018
Mg .002	.010
K .012	.034
Ca .112	.178

Maple Leaf*

Volume Weighted Average	Linear Average
Na (-.022)	.008
Mg .004	.012
K .015	.042
Ca .094	.154

Tolt River

Volume Weighted Average	Linear Average
Na (-.003)	.024
Mg .006	.007
K .020	.032
Ca .037	.049

Appendix E

King County Emission Inventory (tons/yr), 1980

Source	SOx	NOx
Fuel Combustion	22024	8700
Industrial Processes	640	1052
Solid Waste Disposal	1	2
Transportation	3091	41796
Slash burning		67
King County Total	25756 tons/yr	51617 tons/yr

Pierce County Emission Inventory, 1980

Source	SOx	NOx
1. Fuel Combustion	12102	6808
2. Industrial Processes	88351	175
3. Solid Waste Disposal	2	3
4. Transportation	1186	14575
5. Slash burning	1	26
Pierce County Total	101,642 tons/yr	21,587 tons/yr

1980 Two County SOx and NOx Emissions

	SOx	NOx
King	25,756	51,617
Pierce	101,642	21,587
Total	127,398	73,204 tons/yr

1979 Four County SOx and NOx Emission

King, Pierce, Kitsap and Snohomish Counties

SOx	NOx
136,195	92,313

King and Pierce Counties, Percent of 4 County Total:

SOx = 93.5%

NOx = 79.3%

Comparison of Major Point Sources to Two County Total Emission

1. Auto/Transportation (NOx)= 14,575 Pierce

41,796 King

56,371 tons/year

77% of 2 County NOx = transportation

2. Smelter (SO2) = 87,178 tons/yr

68% of 2 County SO2 = Smelter

Appendix F

PROCEDURES FOR ACID RAIN SAMPLING

1. Scrub the inside of the collection bucket and lid, using a new or very clean brush which will be set aside and used only for this purpose. Disposable kimwipes may also be used. No tap water or soaps should ever be used on any acid rain equipment. Only deionized water shall be used and the conductivity of the deionized water should be less than or equal to 1.5 umhos/cm. This check should be made before any washing or rinsing is started. A small amount of baking soda can be used as an aid in scrubbing. When scrubbing is completed, rinse the bucket and lid with deionized water at least three times.

   NOTE: To develop proper field and lab technique, great care should be taken to prevent touching the inner surface and rim of the bucket and lid. Disposable plastic gloves are reocmmended for in-lab work with the buckets to prevent accidental contact while scrubbing. For the same reason, the lid should always be set down with the inside up.

2. After scrubbing and rinsing the bucket is ready for the acid rinse. Add a workable amount of 0.5 N HCl and carefully swirl. The dilute acid should contact the entire inner surface of the bucket. Let stand for 15 minutes. Slowly empty while turning the bucket to once again cover the entire inner surface and the entire rim of the bucket. Rinse thoroughly at least three times with deionized water contacting all inner surfaces and entire rim. Allow the last rinse to sit in the bucket for at least one hour. At the end of this time, check the conductivity of the last rinse water. If the conductivity is greater than 1.5 umhos/cm., repeat the deionized water rinse process. If the conductivity is less than or equal to 1.5 umhos/cm, save an aliquot of the final rinse in a new and previously (deionized water) rinsed Nalgene sample bottle. Label this last rinse sample as it is to be analyzed as a background for the rain sample later collected in that bucket.

   NOTE: Use only reagent grade hydrochloric acid for the acid rinse. The bucket lid does not go through the acid rinse process as it might damage the sealing gasket.

3. Check the conductivity of the deionized water before filling the carboy and after the water comes out of the carboy spigot. The readings should both be less than or equal to 1.5 umhos/cm. and no more than a 10% difference between the two readings. Sample bottles (new Nalgene only) should be rinsed in the lab, using only water from the carboy as this is the only water source in the field. Rinsing of the sample funnel and graduate cylinder between samples should be done only with water from the carboy. The "clean" or sample funnel and graduate cylinder should be kept separate from other equipment and stored in a clean plastic bag during transportation and storage to prevent contamination.

FIELD PROCEDURES FOR ACID RAIN SAMPLING

1. Check sampler operation. If closed, use a piece of metal to short the sensor; it should open. If it is raining at the time of collection and the sampler is open, remove the water from the sensor; it should close. Note the status of sampler (open/closed), operability, weather conditions, date and time. Carefully remove wet-side sample bucket and repalce with clean acid-rinsed bucket. Put the lid from the clean bucket on the just removed wet-side bucket and carry the covered sample to the van to prevent spillage or contamination. When handling the sample buckets and lids, care must be taken to avoid touching any surface that may eventually come into contact with the sample.

2. Remove the chart paper from the rain gauge. Record the time and date on the chart paper. Using the "dirty" or non-sample graduate cylinder (and funnel if desired), measure the volume of the rain gauge sample and record this on the chart paper. Do the same with dry-side bucket of the sampler. These samples are discarded. Replace the rain gauge chart paper carefully, wind the gauge chart drive timer (do not overwind) and refill the pen with ink if needed. The chart must start on Monday to enable the gauge to record properly for seven days. We will be collecting on Tuesdays, but any corrections will be made later. Do not engage new chart until the guage bucket has been emptied. Engage pen to new chart and add a starting spike with the pen to ensure proper ink flow. Close the door to the rain gauge housing and make sure the lid to the rain gauge is secure.

3. Carefully replace sampler batteries with freshly charged batteries. Disengage both used batteries, taking care to prevent shorting the battery by touching contacts, and remove. Place fresh batteries in position and carefully attach leads to posts. Replace and secure battery lids. Finally, check to see that sampler is operational.

4. While in the van, record in a bound log book the information previously recorded on the rain gauge chart paper. Do this while your field conductivity meter is warming up. Also record the sampler status (open/closed), operability and weather conditions. Record also the field measurements about to be taken. Make a note of the condition of the actual sample, looking for dust or soil particles, leaves, bugs, bird excrement, a ring in the bucket or anything notable. Remove the "clean" graduate cylinder and funnel from plastic bag and rinse with water from the carboy. Rinse all inner surfaces of the graduate and slowly rotate while emptying to rinse the entire rim. Carefully handle only the outside surface of the funnel while rinsing and only the upper portion of the funnel as the outside surface of the spout will contact the sample when filling the sample bottles. Be sure to rinse the outside of the spout too. Rinse the graduate and funnel three times. Do not empty the last rinse from the graduate. Place the rinsed funnel upsdie down on the inside surface of the lid to the collection bucket. The bucket lid, as well as all other caps and lids, should be at rest with the inside (sample

contact) surface up.

Rinse the conductivity probe and tube used for measurements several times and then take a reading. The conductivity of the rinse water should be less than or equal to 1.5 umhos/cm, and within 10% of the blank. Record the measurement and temperature. Measure and record the values of the conductivity standards, being sure to include temperature readings. Whenever conductivity standard measurements are taken, start with the lower standard first and rinse the probe and tube between standards. The probe and tube should be rinsed between all readings and the probe should be submersed and shaken dry several times before a reading is taken. Rinse the probe and tube and then take a reading from the last rinse of the "clean" graduate cylinder. Once again, the conductivity should be less than or equal to 1.5 umhos and within 10% of the blank. Empty the graduate, rinsing the entire rim as you do so. Using the funnel, carefully measure the volume of the rain sample in the graduate. Read and record the volume to the nearest 10 milliliters, Using the funnel fill pre-rinsed 8 oz. Nalgene sample bottles, two for the EPA lab, one for the WDOE lab in Olympia and sample permitting one for your own use. Seal and label sample bottles. Measure and record conductivity and temperature of remaining sample using the same dunk and shake technique. Repeat if sufficient sample allows. Rinse the probe and tube and take known standard measurements once again and record. If sample quantity is limited ,the field measurements and EPA lab aliquots are high priority.

5. Send last rinse sample and all field samples for EPA and WDOE by Greyhound bus (collect) to: Washington Department of Ecology
Mail Stop PV-11
Olympia, WA 98504

If sample quantity allowed, and you have an aliquot of your own, allow the sample to reach room temperature (20 - 25°C) and measure pH, conductivity and temperature and record in the log book. Store and ship samples at 4°C.